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HIGH TEMPERATURE WINDSHIELD/CANOPY MATERIALS DEVELOPMENT

DR. G. J. SCHMITT
DR. D. C. PREVORSEK
DR. B. T. DEBONA

ALLIED CHEMICAL CORPORATION
CORPORATE RESEARCH CENTER
MORRISTOWN, NJ 07960

AUGUST 1980

TECHNICAL REPORT AFML-TR-79-4221
For Period 15 October 1978 to 14 October 1979

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EDWARD A ARVAY,
Project Monitor

T. J. REINHART, JR., Chief
Composites, Adhesives & Fibrous
Materials Branch
Nonmetallic Materials Division

FOR THE COMMANDER

Franklin D Cherry

FRANKLIN D. CHERRY, Chief
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This report covers the first year of work on the program to develop new, high temperature stable, transparent plastics for use in high performance aircraft as materials of construction for windshields and/or canopies. Thirty novel materials were prepared during this period, each with a glass transition temperature exceeding those of currently used acrylic and polycarbonate plastics, and possessing varying degrees of transparency, color, and impact strength. Substitution of thermally stable, aromatic diols and diacids by appropriate techniques for bisphenol-A in established preparatory procedures for polycarbonates

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and polyesters has resulted in the more thermally stable materials. Depending upon the reactants involved, new polyesters, polycarbonates, polyester carbonates, copolyesters and copolyester carbonates have been prepared. Materials based upon tetramethyl dicumyl bisphenol (coded AF-TP-2) have glass transition temperatures (Tg) ranging from 190 to 228°C (374°F to 442°F); light transmittance is generally over 80%; however, haze is rather high, the yellowness index is high, and the impact strength (notched izod) is between 1.0 to 3.0 ft-lb per inch of notch. Materials based upon combinations of tetramethyl dicumyl bisphenol, bisphenol-A, tetraphthoyl chloride and phosgene also possess desirable properties. Properties of many of the materials have been determined while others are still in progress.

FOREWORD

This report was prepared by Allied Chemical Corporation, Corporate Research Laboratory, Morristown, NJ 07960 under Air Force Contract F33615-78-C-5077 entitled "High Temperature Windshield/Canopy Materials Development". The Contract was initiated under Project NR. 2423, "Electromagnetic Windows and Materials", Task NR. 242302, "Windshields and Canopies".

The work is sponsored by the Air Force Materials Laboratory, Nonmetallic Materials Division, WPAFB, Ohio, under the direction of Mr. E. Arvay (AFML/MBC) as Project Monitor.

Efforts at Allied are being conducted within the Polymer Science Department under the direction of Dr. G.J. Schmitt, Department Manager. Dr. D.C. Prevorsek is the Project Manager and Dr. B.T. DeBona the Principal Research Chemist. Laboratory support has been provided by Mrs. E. Dougherty, Ms. J. Maccari and the staff of the Analytical Department. Mr. W.K. Stemple has acted as Government Liaison.

This report covers the period 15 October 1978 through 14 October 1979.

Submitted on 12 Decmeber 1979 and the revised draft on 4 August 1980

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1.0 INTRODUCTION

During the last decade there has been an increasing need for improved materials of construction for advanced aircraft that operate at supersonic speeds. One materials area in which considerable deficiencies continue to exist is the transparencies of windshield - canopy assemblies. Several requirements for these transparencies are thermal stability, resistance to bird impact, abrasion resistance and optical clarity. While glass transparencies have adequate thermal resistance properties, various deficiencies such as the weight of the finished part, brittleness and fabrication problems are apparent. In addition, glass structures generally do not have sufficient impact resistance to withstand damage from bird strikes.

Over the years polymer science and technology has provided the means of overcoming many of the deficiences of glass transparencies. Such properties as low density, impact strength and optical clarity have been relatively easily achieved with several synthetic plastics. However, the existing plastics which meet requirements of transparency and impact strength do not have sufficient heat resistance for windshield - canopy applications in advanced aircraft. Two noteworthy examples are acrylics and bisphenol-A polycarbonate. In the case of acrylics the service limit is about 250°F (121°C). With polycarbonate dimensional stability can be maintained up to about 300°F (149°C) for short time periods. Since the windshield - canopy structures of advanced aircraft can reach temperatures as high as 450°F (232°C), the need for a more thermally resistant plastic having the required optical clarity, impact resistance, abrasion resistance and processability is clearly evident.

During the past several years Allied Chemical Corporation has been involved in an extensive program aimed at the development of a family of novel engineering thermoplastics having higher heat distortion temperatures than conventional polycarbonates. The primary member of this series is a polyestercarbonate copolymer which has a heat distortion temperature of about 350°F (177°C), good optical properties, high impact resistance and is processable with conventional equipment. Unlike biphenol-A polycarbonate this material does not undergo thermal embrittlement which is a serious problem for any application requiring the retention of impact strength after heating cycles. This polyestercarbonate comes very close to meeting the major target objectives for advanced aircraft transparencies. The only shortcoming of the material is the heat distortion temperature.

The main objective of this program has been the development of analogs of the polyestercarbonate which embody all the target properties and in particular an increase in the heat distortion temperature of about 50 to 100°F (25 to 50°C). The technical approach employed to arrive at suitable materials has involved primarily a selective structural redesign of the monomeric components comprising the polyestercarbonate.

2.0 SUMMARY

At this time twenty four polymer systems have been developed employing the selective structural redesign of the medium temperature capability polyestercarbonate. These materials fall primarily into two classes which represent separate and highly selective chemical modifications to the components of the polyestercarbonate. In many cases new reaction chemistry or significant modification of existing processes have been successfully developed. Of these twenty four polymer candidates, three exhibit improved properties over the original polyestercarbonate.

The first of the three candidates involves complete modification of the aromatic diol component and is designated as AF-TP-2. This material contains O,O,O', O'- tetramethyldicumylbisphenol (TMDCB) as the sole diol component which functions to increase the stiffness of the polymer chain and thus raise the heat distortion temperature. The second candidate is designated as AF-TP-6, and is the result of a partial replacement of the diol component in the parent polyestercarbonate by TMDCB. The third candidate, AF-TP-9 is a polyarylate in which both diacids of the polyestercarbonate are replaced by 4, 4' - benzophenone dicarboxylic acid (BDA).

These candidates come close to the program targets in terms of higher heat distortion or glass transition temperatures (392-410°F, 200-210°C). Mechanical properties such as yield elongation,

yield strength, ultimate elongation, ultimate tensile strength and modulus were measured and in most cases approach or meet the target objectives. Work-to-failure as reflected by notched IZOD impact mesurements were the highest for AF-TP-9. AF-TP-2 and 6 showed lower notched IZOD values. Unnotched IZOD measurements were similar for the three materials. Optical properties were assessed by transmittance, haze and color measurements of molded specimens. Although AF-TP-2 and 6 come close to the target values, all AF-TP-9 preparations have yielded high color values. Compression molded specimens of AF-TP-2 and 6 demonstrated remarkable resistance to hydrolysis by both strong hot aqueous acid and base in comparison to reference materials. Information on the processing characteristics of the three candidates was obtained from compression molding studies. In terms of these characteristics the three behave in a manner similar to the polyestercarbonate.

3.0 TECHNICAL DISCUSSION

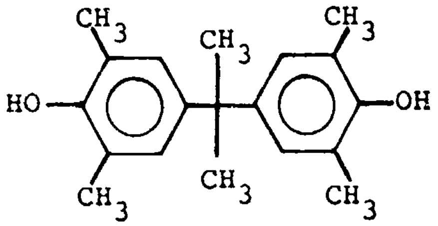
3.1 Structural Modification of Diol

One approach to improving the properties of the polyester-carbonate was the investigation of analogous polymer systems having the aromatic ring positions ortho to the carbonate or ester linkages substituted by alkyl groups. Such substitution is known to result in attenuation of the inherent flexibility of the carbonate or ester linkages which in general is manifested by an increase in the glass transition temperature, Tg, of the substituted vs. unsubstituted polymer. In addition the proximity of alkyl substituents ortho to the carbonate or ester linkage provides a steric "shielding" which effectively enhances the overall hydrolytic stability of the polymer, especially polycarbonates.

Although the above approach was expected to raise the Tg above 200°C and provide greater hydrolytic stability, two important difficulties were anticipated as a direct result of the steric bulk of the substituents. The first was the difficulty in attaining high molecular weight polymer in solution polycondensations; the second and more important was the adverse effect on mechanical properties.

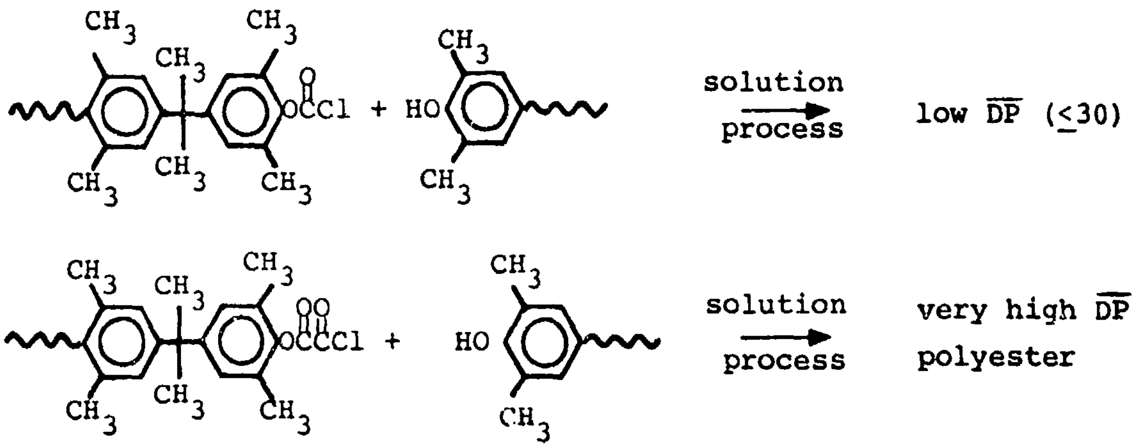
A preliminary investigation of this approach provided necessary information with respect to Tg and mechanical property changes. The likelihood that suitable additional structural modifications along with the basic approach could suffice to raise Tg without seriously comprising mechanical properties was also assessed.

3.1.1 Polymers of Tetramethylbisphenol-A (TMBA) - AF-TP-1 Series



(TMBA)

In the earliest stages of investigation it was found that the reaction of TMBA in solution with phosgene leads only to oligomeric polycarbonate even in the presence of such "hypernucleophilic" catalysts as 4-N, N-dimethylaminopyridine. The literature indicated that the lack of "reactivity" of TMBA is governed by both steric hindrance and high basicity of the hydroxyl groups. However, it was demonstrated that exceedingly high molecular weight ($[\eta] = 4$) polyester could be synthesized with oxalyl chloride by normal solution polycondensation with pyridine as both acid acceptor and catalyst. In addition it was shown that both intermediate chloroformates as well as half ester-acid chlorides form readily in solution processes, and it is the reaction of TMBA hydroxyl end groups with the intermediate chloroformate which presents the obstacle to the attainment of high molecular weight polycarbonate.



Thus, on the basis of extending the reactive carboxyl chloride one carbon atom in bond length from the bulky substituents, it was concluded that steric hindrance rather than any inherent lack of hydroxyl reactivity was the predominant factor limiting polycarbonate synthesis in solution.

On the basis of the above chemistry methods for preparation of high molecular weight polycarbonates, polyesters and polyester-carbonates of TMBA were devised. In the case of polyesters derived, for example, from unsubstituted aromatic and aliphatic acid chlorides, solution polycondensation in the presence of tertiary amine catalysts was sufficient for attainment of high molecular weight. In contrast, polycarbonates had to be prepared by activating the hindered hydroxyl groups enough to overcome the steric boundary. This was conveniently accomplished by converting the hydroxyls to phenoxide anion in what is essentially a two-stage interfacial polycondensation. The procedures have also been extended to allow for preparation of polyestercarbonate copolymers (acid chloride and phosgene) by a two stage one pot process. By utilization of these techniques the entire range of copolymer composition was easily obtainable in which the monomer ratios in the final polymer were the same as the monomer feed ratios.

As part of our preliminary investigation the following polymers were prepared from TMBA:

Oxalate ester (AF-TP-1)
Terephthalate ester (AF-TP-1A)
Carbonate ester (AF-TP-1B and 1B-1)
Terephthalate-Carbonate ester (AF-TP-1C)

The polyestercarbonate of TMBA (AF-TP-1C) served as the "ortho alkyl substituted" analog of the reference polyestercarbonate. The others were important not only in their own right as potential candidates but also as controls for property evaluations as well as developing the chemistry described above.

In order to assess the viability of the TMBA modifications, evaluation of a few critical properties was undertaken. Among these were the evaluation of glass transition temperatures (Tg), decomposition temperatures (TGA), processability (compression molding), and some qualitative indication of mechanical properties (ductility). Some pertinent data for these polymers is shown in Table 1.

TABLE 1. POLYMERS OF TETRAMETHYLBISPHENOL-A (TMBA)

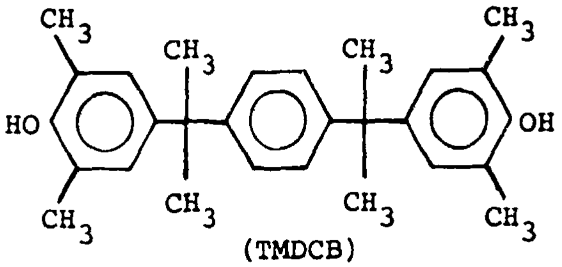
Designation	Type	η_{sp}/C*	Tg(°C)	TGA(°C)	Ductility
AF-TP-1	Oxalate	4.0	153	>350	---
AF-TP-1A	TPA ester	1.9	253	>400	Brittle
AF-TP-1B	Carbonate	0.87	195	"	Brittle
AF-TP-1B-1	Carbonate	1.23	200	"	Brittle
AF-TP-1C	TPA-Carbonate	1.43	223	"	Somewhat Brittle

* C = 0.5, phenol-TCE, 25°C

Of these five materials only AF-TP-1C appeared suitable for further study. The others were either so brittle after compression molding that flexing of 40 mil sheet beyond 30°∡ resulted in failure or the Tg value was too low. Since AF-TP-1C did not appear as brittle as the others, tensile specimens were evaluated. Although the modulus was sufficiently high (295,490 psi), the ultimate elongation and tensile strength were poor (7.4%, 6,690 psi, respectively) in comparison to conventional high performance plastics.

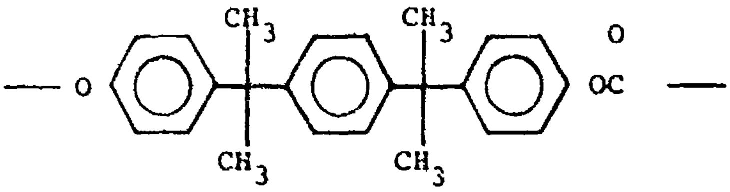
3.1.2 Further Structural Modification of TMBA

In order to further identify some molecular-structural factors responsible for the poor elongation properties of AF-TP-1C an investigation of some related polymers based on ortho-substituted dicumyl bisphenols was initiated. The primary one under consideration, represented by the structure



(TMDCB)

is essentially a structural modification of TMBA. The reason for this choice was two-fold. Reduction of the inherent flexibility of the carbonate or ester linkages by ortho-substitution while desirably raising the Tg of polycarbonates and polyestercarbonates was also recognized as a factor which seriously lowers the ductility. Thus, a beneficial modification would be one in which a number of carbonate or ester linkages is replaced with a unit which is known to keep the Tg within the necessary range without sacrifice in mechanical properties. There was ample evidence to indicate that the dicumyl bisphenol structure would meet these requirements, since mechanical properties as well as Tg of the corresponding polycarbonate are quite similar to those of bisphenol-A polycarbonate.

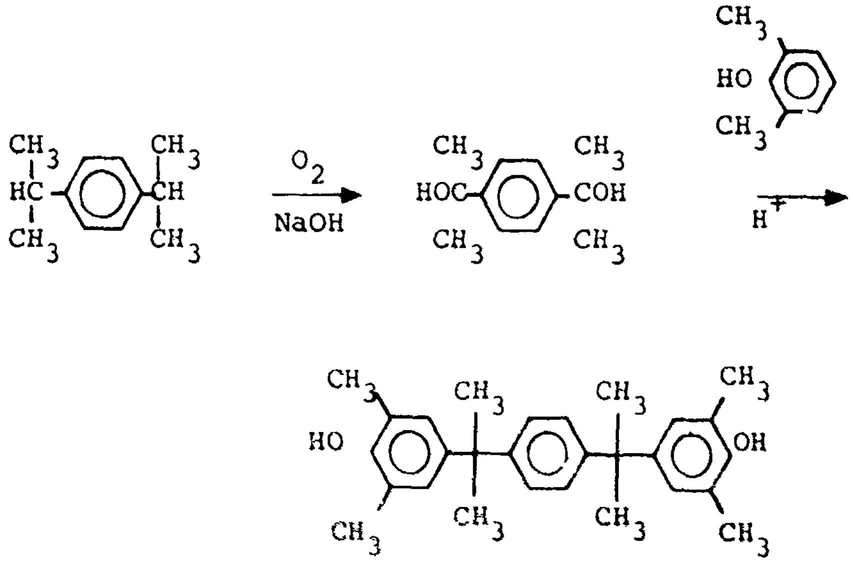


(DCB Polycarbonate)

By examining the effects on mechanical properties of ortho-substitution in polymers derived from dicumyl bisphenols, a qualitative assessment of the importance of carbonate or ester flexibility vs that of structural modification between the phenolic rings would be possible.

3.1.3 Synthesis of 0,0,0',0' - Tetramethyldicumylbisphenol (TMDCB)

The monomer synthesis was accomplished by starting with p-diisopropyl benzene as presented in the following scheme:

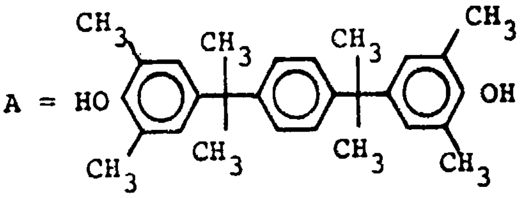


(TMDCB)

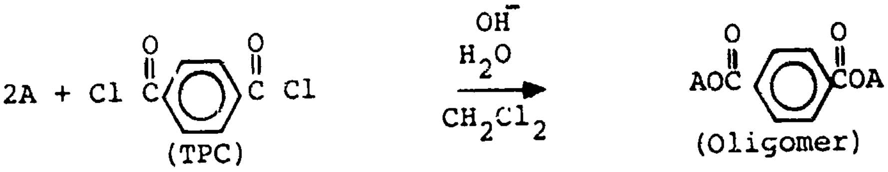
The reaction was conducted in two steps with purification of the intermediate p-diisopropyl benzene - α,α'-diol by recrystallization. The yield of highly pure TMDCB monomer after two recrystallizations averaged over many runs was 50% based on starting diol. (See Section 7.1, Preparation of Intermediates and Monomers)

3.1.4 Polymers Based on TMDCB - AF-TP-2 Series

Initially the synthesis of TMDCB polyestercarbonates derived from terephthaloyl chloride (TPC) and phosgene (Phg) was conducted by a two-stage interfacial polycondensation entirely analogous to that of the corresponding TMBA polyestercarbonate. The first member of this series, AF-TP-2, was prepared having a molar composition of 2:1:1 TMDCB/TPC/Phg in the feed. In the first step of the reaction sequence a slurry of aqueous base and TMDCB powder was reacted with terephthaloyl chloride dissolved in dichloromethane. The mixture of polyester oligomers formed was then reacted with phosgene gas under basic conditions. High molecular weight polyestercarbonates resulted only when a "catalytic" amount of triethylamine was present in the reaction mixture. Only low $\overline{DP}$ products were obtained when either no triethylamine was present or when the amine was present in excess of 15 mole % based on TMDCB. The reaction sequence for this two-stage interfacial process is illustrated below.



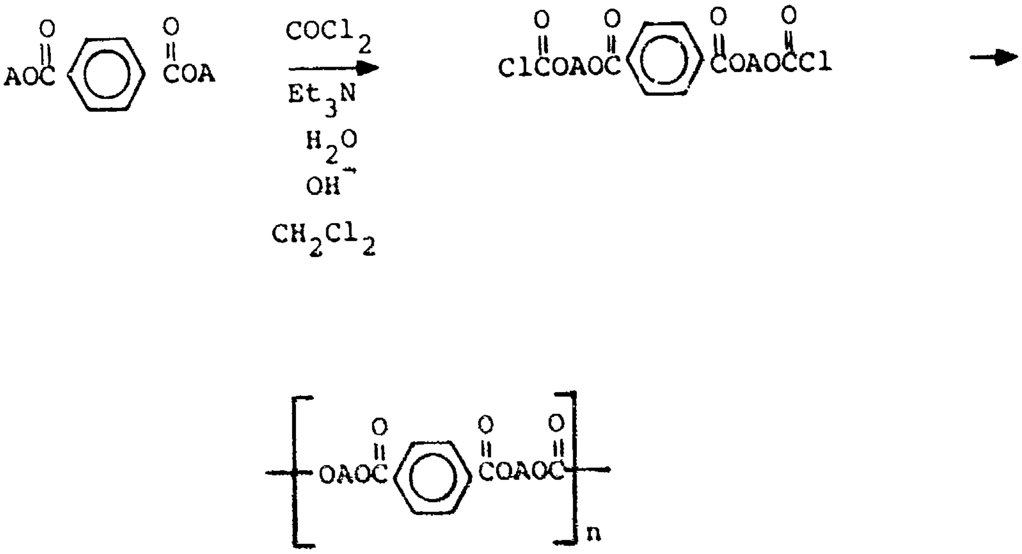
STAGE 1



(TPC)

(Oligomer)

STAGE II



(AF-TP-2)

The first stage of the process involved the preparation of low molecular weight hydroxyl terminated oligomer by the interfacial technique, followed by addition of phosgene to form chloroformate terminated oligomers which then undergo polycondensation to the final product. The above equation for the two-stage scheme shows the "idealized" alternating co-polyestercarbonate resulting from a 2:1 feed ratio of TMDCB:TPC. However, the actual situation is somewhat more complicated. Under the conditions of complete reaction and with the assumption of a most probable distribution, a 2:1 feed ratio of monomers should give rise to a distribution of oligomers of the type $(AB)_nA$; where, on a number average basis, $\eta = 0$ accounts for 50% of the molecules (i.e., pure A) and $\eta = 1,2,3,4...$ accounts for the remaining $(AB)_nA$ oligomers.[1] It has been demonstrated that this analysis very accurately describes the situation encountered in the reaction of bisphenol-A with TPC at 2:1 ratio in a solution process. In this case, the weight contribution of oligomers for which η is beyond 5 is insignificant.[2]

In the interfacial process described above, the bulk of the TMDCB was initially considerably insoluble in both the aqueous base and the dichloromethane. However, the monomer gradually dissolved as reaction with TPC proceeded, since the final oligomers were quite soluble in the organic phase. Thus, the partial solubility of the monomer was certain to distort the distribution of oligomers. Although the distribution of oligomers was not measured in this case, some evidence for high $\overline{DP}$ values was obtained. Results in Table 2 show a comparison of reduced specific viscosities for oligomers prepared from TMDCB and TPC by both interfacial and solution processes. It is apparent that for the interfacial process in the vicinity of the interface, there must be a reactant ratio closer to 1:1 which gives rise to higher $\overline{DP}$ polyester oligomer.

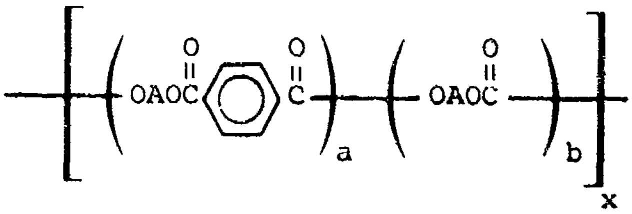
TABLE 2. VALUES OF REDUCED SPECIFIC VISCOSITY FOR OLIGOMERS OF TMDCB-TPC PREPARED BY INTERFACIAL AND SOLUTION PROCESSES

Entry	Mole Ratio TMDCB/TPC	Process	Reaction Time, Temp.	η_{sp}/C (CH_2Cl_2)
1	2:1	IF	5 min., 25°C	0.11
2	2:1	IF	10 min., 25°C	0.18
3	2:1	IF	20 min., 25°C	0.19
4	2:1	IF[a]	30 min., 25°C	0.22
5	2:1	S[b]	20 min., 25°C	0.05
6	2:1	S	90 min., 25°C	0.08
7	2:1	S	240 min., 25°C	0.08

[a] TPC solution added over a 10 minute period to the slurry of TMDCB in aqueous base.

[b] Homogeneous solution of reagents in pyridine-dichloromethane

Therefore, on the basis of the results shown in Table 2 and the theoretical calculations of oligomer distribution, the structure of the final AF-TP-2 prepared by the two-stage interfacial process is more accurately represented as:



where the values for "a" (polyester) and "b" (polycarbonate) blocks are fairly small but probably greater than the corresponding values for those of the reference polyestercarbonate.

3.1.5 Molecular Weight Control - AF-TP-2 Series

During the initial phases of the program, considerable attention was given to control of the final molecular weight for the polymer prepared by the two stage interfacial process. This control was considered to be of great importance, since the ease of melt processing depends to a great extent on molecular weight. Initial experiments, in which high purity reagents were employed, consistently gave polymers of extremely high molecular weight. In many cases, reduced specific viscosities for AF-TP-2 type polymers were well over 4 dl/g which probably corresponds to over 100,000 molecular weight. Such high molecular weights would create serious melt processing problems. Experience indicated that values of reduced specific viscosities in the range of 0.6 to 1.8 dl/g would be more satisfactory.

In the initial work with the interfacial polycondensation stage for AF-TP-2, it was observed that at least two methods of molecular weight control were theoretically applicable. The first method is a direct result of the rather slow molecular weight rise during the polycondensation which is illustrated in Figure 1.

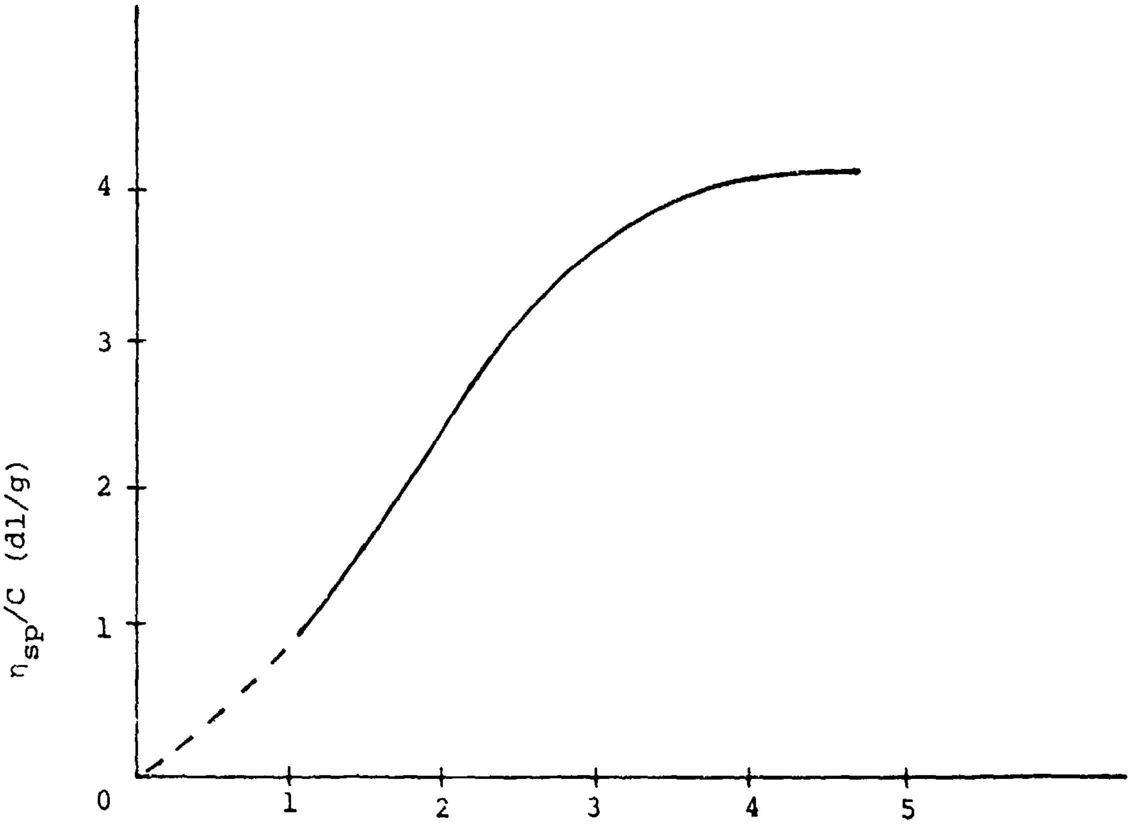


FIGURE 1. Variation of Reduced Specific Viscosity with Polycondensation Time for AF-TP-2 Preparations without Regulator

The curve in this figure depicts the rise in polymer viscosity as polycondensation proceeded in the absence of chain terminators and at pH=12. With the use of a suitable viscosity monitoring device coupled directly to the reaction vessel, one could, in principle, stop the reaction at any chosen value of ηsp/C by addition of an appropriate chain terminator. The other method which is more easily employed on a laboratory scale is the addition of chain regulators before the start of the polycondensation stage. For this method a calibration curve was necessary in order to relate the amount of regulator to the final polymer viscosity, since in interfacial systems calculation of final molecular weight from the mole ratio of monomers to regulator is generally not possible.[3]

Good results for the calibration curve were obtained with p-t-butyl phenol as the chain regulator. The curve which is displayed in Figure 2 was derived from small scale preparations of AF-TP-2 in which the regulator was added at the end of the first third of phosgene addition. There is much more scatter in the data points than similar calibrations involving homogeneous solution polycondensations. This scatter is a result among other factors of variations from batch to batch in emulsion droplet size which depends on stirrer and reactor configuration as well as exact speed of stirrer rotation. However, for this work the degree of molecular weight control obtained by this technique is considered adequate. For example, for a target viscosity of 0.8 dl/g, values between about 0.6 and 1.0 can be expected from replicate runs.

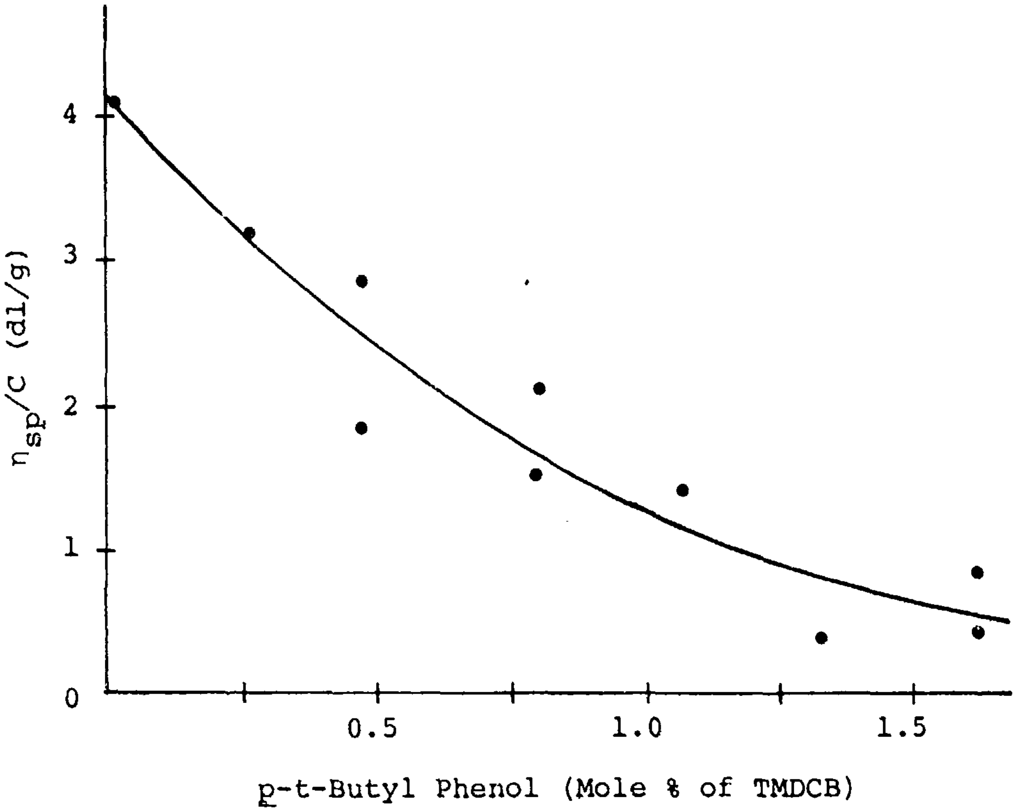


FIGURE 2. Variation of Polymer Reduced Specific Viscosity with Amount of Regulator for AF-TP-2 Prepared by Two-Stage Interfacial Process

An additional feature of the use of a chain terminator which also functions as a stable end-capping reagent in this type of polymerization is the enhancement in thermal stability of the final polymer. Since this polycondensation proceeds through reaction of chloroformate end groups, non end-capped materials will retain some unreacted chloroformate. The chloroformate ends are thermally as well as hydrolytically unstable especially at melt processing temperatures. Thus, in addition to employing the p-t-butyl phenol as a regulator during polycondensation, it was found advantageous to add additional quantities of this material at the end of polycondensation. In this manner, any remaining chloroformate ends were converted to the more stable p-t-butyl phenyl carbonate ends. The results in Table 3 show the dramatic effect of regulator and end-capping on both the color and reduction in thermal chain degradation of molded specimens of AF-TP-2. In the cases of regulator added before polycondensation, color and degree of degradation were improved over unregulated polymer, but these properties were still unsatisfactory, since the molding conditions employed would be typical processing conditions for this material. However, in the cases of polymer prepared with regulator added as usual, but with additional p-t-butyl phenol added at the end of polycondensation, color is greatly improved and there is no chain degradation.

TABLE 3 EFFECT OF REGULATOR AND END-CAPPING ON THERMAL DEGRADATION

Entry (AF-TP-2)	η_{sp}/C (Powder)[a]	η_{sp}/C (molded)[b]	Color
1 (Unregulated)	2.30	1.30	Yellow
2 (Unregulated)	0.82	0.53	Yellow
3 (Regulated)	1.15	0.93	Light Yellow
4 (Regulated)	0.92	0.80	Light Yellow
5 (Regulated and end capped)	1.0	0.91	Very Light Yellow
6 (Regulated and end capped)	1.09	1.09	Very Light Yellow

[a] Freshly precipitated and dried

[b] Molded at 320°C for 10 minutes

3.1.6 Combination Solution - Interfacial Polycondensation Method for AF-TP-2 Series

Initially, all experiments on the two stage interfacial polycondensation technique described above for AF-TP-2 were conducted on a fairly small laboratory scale (25-50 g polymer) in order to make best use of our supply of monomer. After successful monomer scale-up, polymerization scale-up (150-200 g) was attempted using the same process. Two problems were immediately encountered as a result of polymerization scale-up. The first involved unexpected troublesome purification of the polymer. It was observed that on a small laboratory scale the polymer phase obtained after the polycondensation stage could be purified by repeated water washing followed by mild acidification and precipitation of the final polymer in 2-propanol. However, on a larger scale washing of the polymer phase was considerably less efficient as a result of the formation of stable water-polymer solution emulsions. The final polymer showed a tendency to discolor on molding even after exhaustive water washing and multiple precipitation steps. The second problem concerns the development of a slight haze in fairly thick sections of molded polymer (1/8").

Both problems were found to be directly related to the two stage polycondensation process. The washing problem seemed to correlate well with the presence of small amounts of unreacted monomer, which as described previously, remain undissolved in either phase. The tendency for some free monomer to remain unreacted in the larger scale preparations is a direct result of less efficient stirrer-reactor configuration. The problem of a slight haze observable in thicker molded sections of AF-TP-2 has been encountered previously in solution polycondensations of similar polymers. In the latter cases, the haze was identified as polymer rich in terephthalate ester linkages. A similar conjecture for AF-TP-2 is reasonable especially in view of the relatively longer blocks of polyester which appear to be present in polymer derived from the two-stage interfacial polycondensation (see Table 2).

The solution to both the washing and haze problem was to preform the Stage I oligomer by a homogeneous solution process, convert the hydroxyl end groups to chloroformate interfacially and proceed with polycondensation as in the two-stage process. Entries 5, 6 and 7 in Table 2 show that in homogeneous solution the oligomers formed have lower molecular weights than in the interfacial method. For the solution preparations the reactants (TMDCB and TPC) were added to dichloromethane containing a 2-fold molar excess of pyridine (based on TPC). The solutions remained homogeneous throughout the reaction which was conducted at 25°C. The oligomeric product was not isolated, but the solutions were washed to remove excess pyridine and the hydrochloride salt. The clear solutions were then reacted interfacially with phosgene followed by polycondensation. Thus, the combination of solution-interfacial methods leads to polyestercarbonates, which in the case of TMDCB, have shorter polyester sequences than the two-stage interfacial process. The resultant polymer solutions were easily washed and showed no tendency to form troublesome stable emulsions. The final molded polymer also had much less haze than previously noted. These polymers which are still designated AF-TP-2 display no other differences in properties. Values for Tg as well as tensile properties are virtually identical to AF-TP-2 prepared by the two-stage interfacial process.

Although the use of p-t-butyl phenol as a chain regulator and end-capping reagent was equally effective in the solution-interfacial method, a new calibration plot was required. In the absence of any regulator the ultimate molecular weight was found to be much higher in this process. This finding was not surprising, since a much purer system resulted from the washing of the oligomer solution, and it is known that the polycondensation stage is more sensitive to impurities than either oligomer or chloroformate formation. The calibration plot for this process is shown in Figure 3. In this plot, it should be noted that the point labeled "x" is for a large scale laboratory preparation (100-150 g polymer) while the other points are for smaller scale experiments (25-50 g). Again the calibration is sensitive to reactor configuration in terms of kettle shape and stirrer effectiveness.

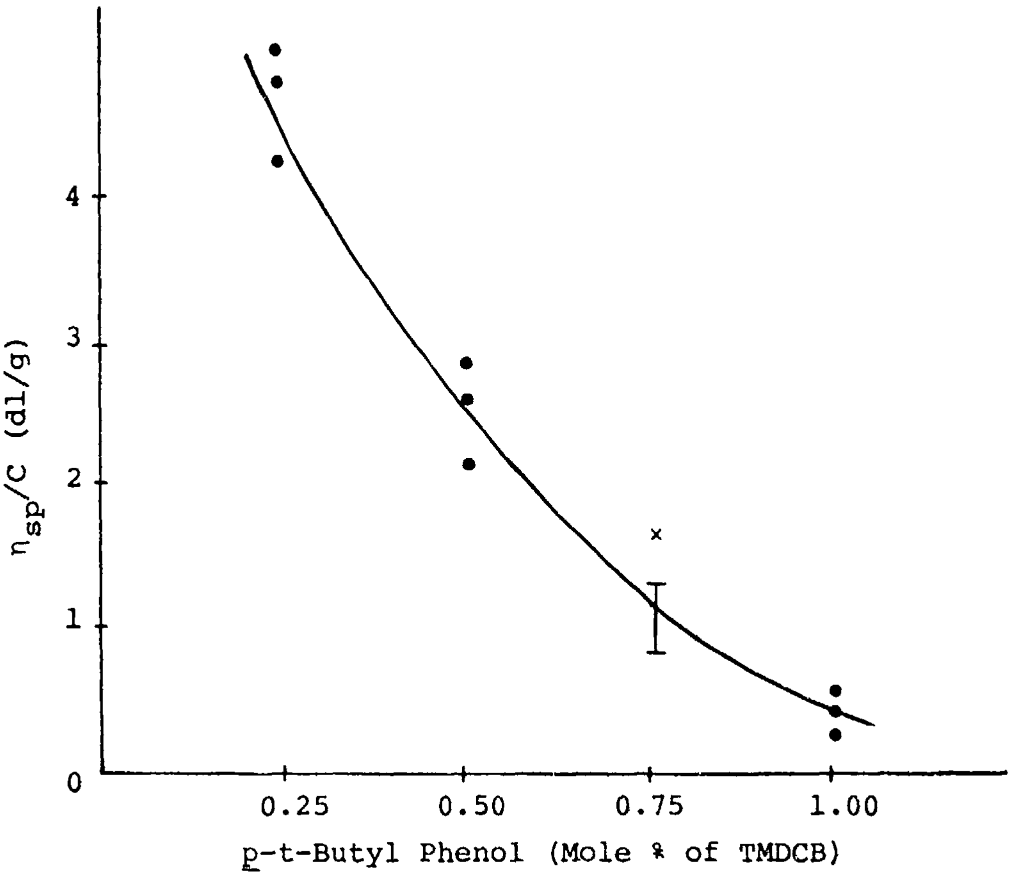


FIGURE 3. Variation of Polymer Reduced Specific Viscosity with Amount of Regulator for AF-TP-2 Prepared by Combination Solution-Interfacial Process

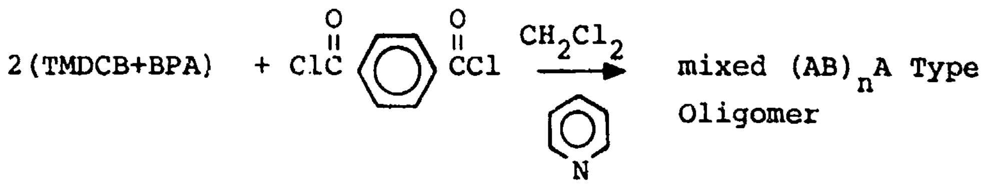
With the combination solution-interfacial approach, polyestercarbonates having ratios other than 2:1:1 for TMDCB, terephthalate and carbonate have been prepared. For example, polymers richer in terephthalate have been successfully prepared by altering the feed ratio of TMDCB/TPC in the oligomer preparation step. For monomer feed ratios between 2:1 and 2:1.5 there was no difficulty; however, at higher TPC values the oligomer solution began to become somewhat heterogeneous as a result of the lower solubility of higher molecular weight polyester in dichloromethane. In any case, polymers containing long polyester blocks appeared to be of little use in this program, since they tended to develop haze upon molding.

3.1.7 Secondary Modification of AF-TP-2 - Copolymerization with Bisphenol-A (AF-TP-3 to 6 Series)

In terms of extending the range in properties of polyester-carbonates based on TMDCB, it was felt that replacement of part of this monomer by bisphenol-A would lead to materials of interest for the program. The objective was to determine the effect of the copolymerized bisphenol-A on the Tg, mechanical properties and solvent and hydrolysis resistance of the final copolymers. From previous experience, good evidence was available that incorporation of some bisphenol-A into AF-TP-2 type polymers should improve some mechanical properties as well as solvent resistance. Such copolymers should also display more favorable melt viscosities which could lead to processing advantages. In this manner, provision could be made for both a choice in the balance of properties and product cost reduction in what would be a family of new high Tg transparencies.

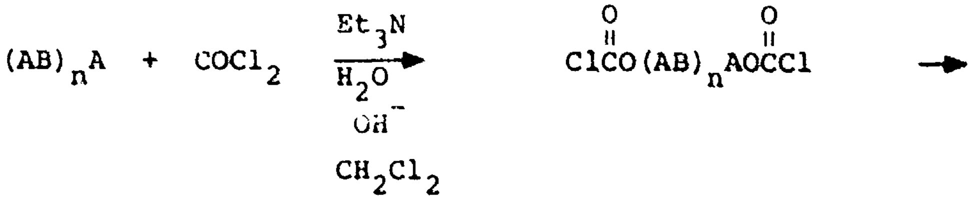
Preparation of a series of co-polyestercarbonates derived from TMDCB, bisphenol-A, TPC and phosgene by the combination solution-interfacial process described previously was successfully accomplished. Copolymers containing up to 60 mole % bisphenol-A (relative to TMDCB) were prepared which gave optically transparent moldings. Copolymers containing up to 30 mole % BPA were prepared by simply mixing both diols in the proper proportions and preforming the mixed $(AB)_nA$ oligomer by the solution process (Step 1). Polycondensation (Step 2) was then conducted in the same manner as for AF-TP-2 preparations.

STEP 1



where A = (TMDCB+BPA)
B = Terephthalate

STEP 2



$$(AB)_nA \;+\; COCl_2 \xrightarrow[\substack{H_2O \\ OH^- \\ CH_2Cl_2}]{Et_3N} Cl\overset{\overset{O}{\|}}{C}O(AB)_nAO\overset{\overset{O}{\|}}{C}Cl \longrightarrow$$

CO-POLYESTERCARBONATE

(mole fraction BPA ≤ 0.3)

These copolymers gave transparent moldings at 320°C. However, by the same technique copolymers richer in BPA showed the development of a slight haze during molding. The formation of haze was traced to the presence of fairly long blocks of bisphenol-A terephthalate in the final polymer as well as unreacted oligomer. During the preparation of oligomers with >30 mole % BPA, some precipitation occurred even in the presence of excess pyridine. The precipitated material, while of acceptably low enough $\overline{DP}$, was richer in BPA than the starting feed mixture. It was shown that during polycondensation much of this insoluble material became incorporated into the polymer. However, enough remained unreacted and dispersed in the polymer phase to give a slightly hazy solution. Although careful filtration sufficed to remove the dispersed oligomer, the presence of long sequences of bisphenol-A terephthalate within the polymer chain still gave rise to haze in final molded samples. Some results of copolymerization experiments are summarized in Table 4, where the cut-off point for acceptable quality polymer (haze free) occurs at 0.7 mole fraction of diol components.

TABLE 4. POLYESTERCARBONATES CONTAINING TMDCB AND BISPHENOL-A

Entry	Composition[a] Monomer Feed	Composition[a] Polymer[b,c]	η_{sp}/C (dl/g)	Tg (°C)
AF-TP-2	1.00	1.00	1.10	210
AF-TP-3	0.90	0.90	1.40	210
AF-TP-4	0.80	0.80	1.10	208
AF-TP-5	0.70	0.70	0.81	205
AF-TP-6-1	0.60	0.65	d	e

[a] Mole fraction defined as TMDCB/(TMDCB + BPA)
[b] Ratio of total diols to terephthalate = 2:1 by IR
[c] Mole fraction TMDCB/(TMDCB + BPA) by NMR
[d] Partially soluble, not measured
[e] Not measured

The problem of haze in copolymers which contained greater than 30 mole % BPA was circumvented by appropriate manipulation of the monomer feed schedule. Thus, for preparations richer in BPA, an oligomer containing 30 mole % BPA was first prepared by the solution technique. The remaining bisphenol-A required for the desired composition was then added. At this point, the oligomer mixture was composed of the mixed TMDCB-BPA terephthalate oligomer along with free TMDCB and BPA monomer. For compositions containing up to 60 mole % BPA, the oligomer solutions remained homogeneous. In addition, all polymer samples were transparent after compression molding at 320°C. Results for preparations involving this improved procedure are summarized in Table 5.

TABLE 5 POLYESTERCARBONATES CONTAINING TMDCB AND BISPHENOL-A (BPA >30 MOLE %)

Entry	Composition[a] Monomer Feed[b]	Composition[a] Polymer[c,d]	η_{sp}/C (dl/g)	Tg (°C)
AF-TP-6	0.60	0.6	1.0	200
AF-TP-6-2	0.50	0.5	0.8	195
AF-TP-6-3	0.40	0.4	0.9	191

[a] Mole fraction defined as TMDCB/(TMDCB + BPA)
[b] Oligomer preparation = 0.70 initially and remainder of BPA at end of reaction
[c] Ratio of total diols to terephthalate = 2:1 by IR
[d] Mole fraction TMDCB/(TMDCB + BPA) by NMR

Laboratory scale-up (150 g) was accomplished for the first entry of Table 5 (AF-TP-6). In this case, the final polymer was identical in all respects to the smaller scale preparation, except that the viscosity of the latter was slightly higher. From Table 5, it can be seen that although haze free copolymers containing 50 and 60 mole % BPA are possible, their limiting Tg values are too low for them to be of any importance in the program.

3.1.8 Other Polymers Derived from TMDCB and DCB

Synthesis of polycarbonates, polyesters and polyestercarbonates based on TMDCB as well as the unsubstituted counterpart DCB (dicumylbisphenol) was carried out with the aim of identifying additional candidate materials bearing the "dicumyl" structural unit. In all cases in which the aromatic diol was TMDCB, interfacial polycondensation methods were required for high molecular weight products. On the other hand polymers containing the DCB unit were preferentially prepared by the solution polycondensation route in which pyridine functioned as the acid acceptor and catalyst. In Table 6 some preliminary data for these materials is summarized.

TABLE 6. POLYMERS DERIVED FROM TMDCB AND DCB

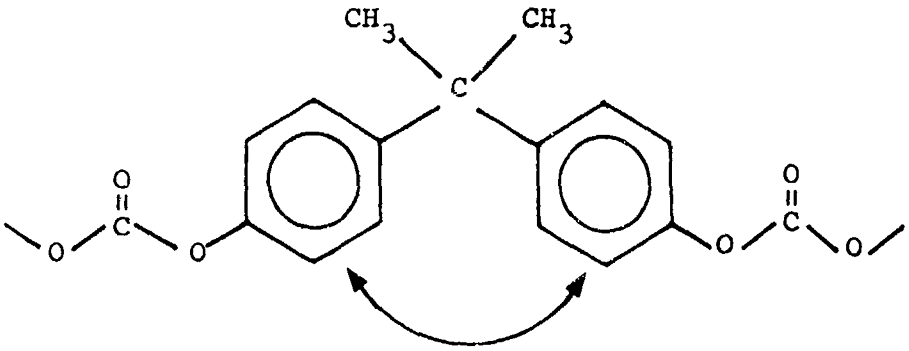
Entry	Type	Composition	η_{sp}/C (dl/g)	Tg (°C)
AF-TP-2A	polycarbonate	TMDCB	1.93	190
AF-TP-2B	polyester	TMDCB-terephthalate	1.01	228
AF-TP-2C	polyester-carbonate	TMDCB 1:1 NDA: Carbonate[a]	0.65	175
AF-TP-7	copolyester	TMDCB 1:1 TP/IP[b]	0.98	212
AF-TP-8	polycarbonate	DCB	1.80	156
AF-TP-8A	polyester	DCB-terephthalate	insol.	NM[c]

a. NDA = 2,6 - naphthalene dicarboxylate
b. TP = terephthalate, IP = isophthalate
c. NM = not measured

All materials shown in the above table were found to be unsuitable as candidates for further study after preliminary evaluation. From the data it can be seen that both polycarbonates of TMDCB and DCB failed to meet the Tg requirement of > 200°C. On a theoretical basis the polyestercarbonate derived from TMDCB and 2,6-naphthalene dicarboxylate should have had a Tg within the target range; however, several repeat experiments failed to yield a Tg substantially greater than 175°C. Impurities in or isomerization of the intermediate acid chloride of 2,6-NDA could be responsible for the low Tg values. The copolyester of TMDCB showed many desirable characteristics including high Tg and good tensile properties; however, this material tended to undergo crystallization as shown by x-ray analysis after compression molding. Crystallization was so severe that pronounced haze could be observed by eye in the molded samples. The DCB terephthalate was so highly crystalline that the material was substantially insoluble in all common solvents. Attempts at forming this material by compression molding were unsuccessful up to 340°C.

3.2 Structural Modification of Diacid

We have hypothesized that the unique characteristics of bisphenol-A polycarbonate (PC), i.e., its high impact resistance and toughness below Tg must be attributed to the geometry of the bisphenol-A group. On the basis of a comprehensive review of polymer properties and molecular structure, we have postulated that the spatial arrangement of the phenylene groups prevents close packing of the polymer coil, which in turn leads to a high degree of chain entanglement as indicated by viscoelastic measurements. We have further speculated that high entanglement also indicates a high degree of chain interpenetration.



We then rationalized that in systems where all other factors except chain interpenetration remain constant, increases in chain entanglement and chain interpenetration should have a positive effect on many mechanical properties such as yield stress and yield strain, dimensional stability under load, impact resistance, etc. This latter assumption was recently verified by the result of M. Hoffman.[4]

Our interpretation of polycarbonate behavior differs considerably from the interpretation proposed in the published literature which attributes high impact strength and ductility below Tg primarily to secondary motions involving the carbonate linkage. Since relatively strong transitions associated with these relaxations appear at about -40°C, it was assumed that PC remains ductile and impact resistant as long as these motions remain activated.

In our judgment, the carbonate group is relatively unimportant in impact resistance but essential for the control of Tg and crystallinity, especially with polyestercarbonates derived from bisphenol-A and terephthalic acid. With this system, the polycarbonate moiety is required to render the polymer melt processable and amorphous.

Using the polycarbonate molecule we can define the structural variables which affect the mechanical and thermal properties of high Tg polymers. These are illustrated in Figure 4.

STIFF SEGMENT LENGTH "L"

CHAIN REDIRECTING GROUPS ◌

PLASTICIZING GROUPS ▨

MAIN CHAIN ANGLE δ

SIDE GROUPS

CHAIN INTERACTION

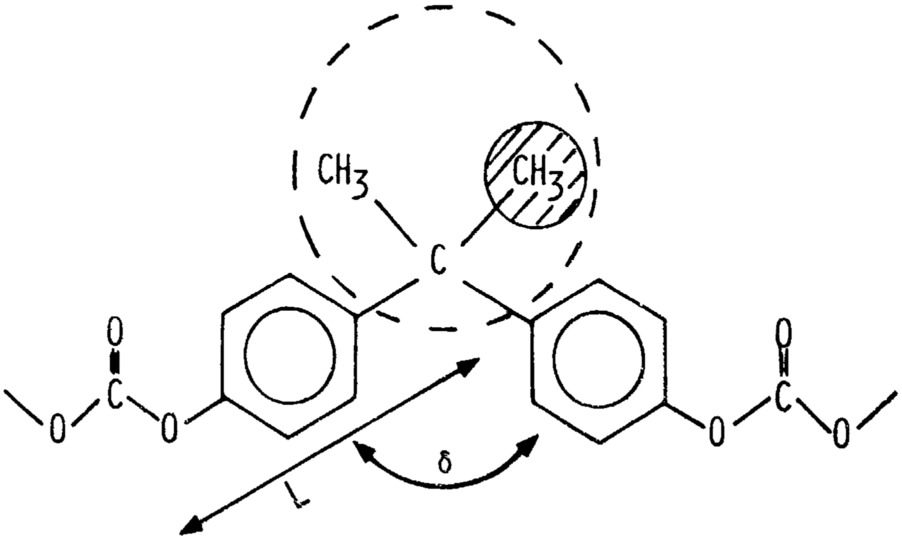
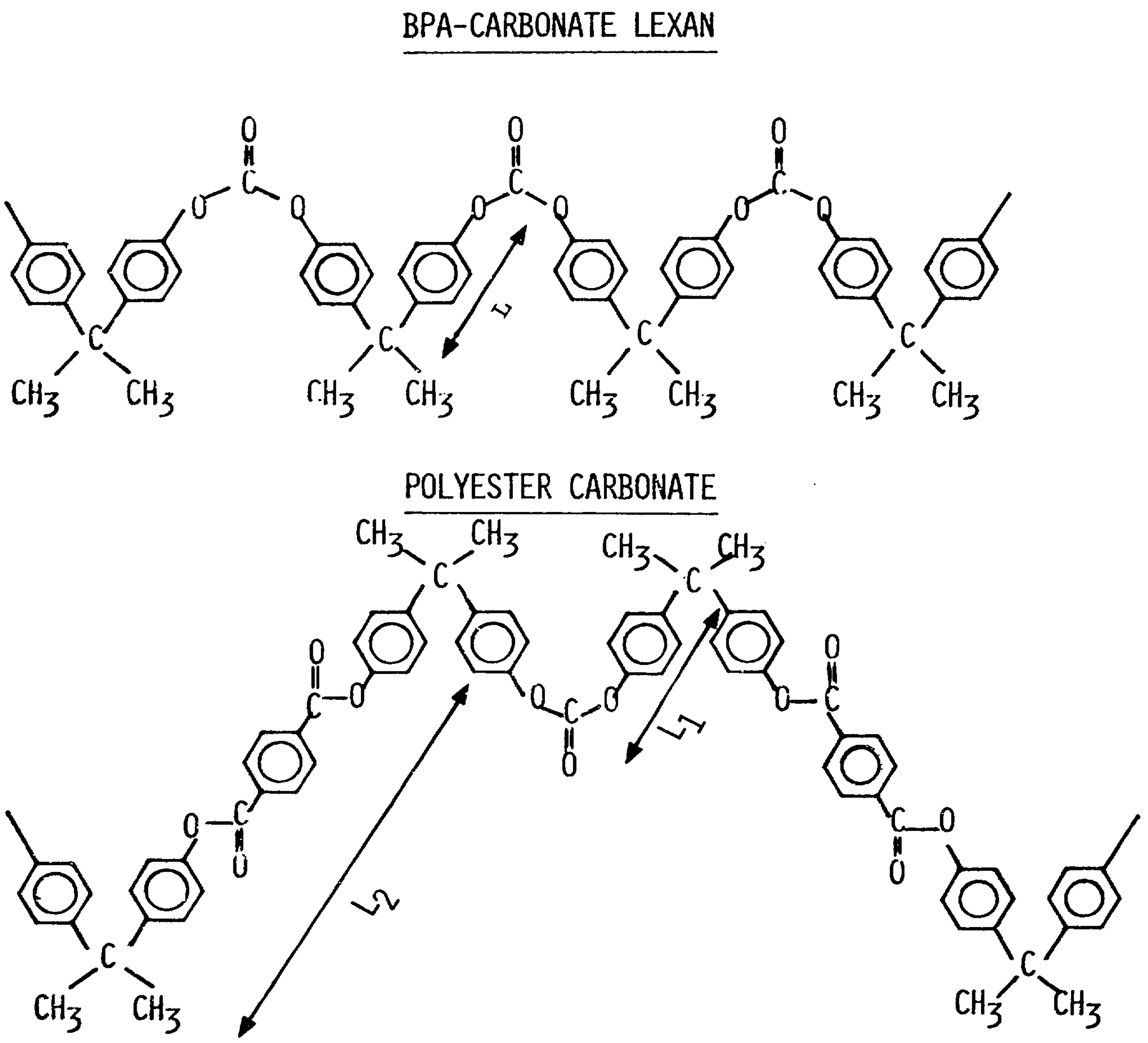


FIGURE 4. Structural Variables Affecting Properties of High T_g Polymers.

For our purposes, the primary concerns were the effects of:

1. Stiff segment length "L".
2. Characteristics of chain redirecting group.
3. Groups affecting packing and free volume.
4. Main chain angle "δ" and its bending force constant.
5. Side groups.
6. Chain interaction (hydrogen bonding, polar groups, etc.)

The effect of an increase in stiff segment length was to some extent established with the reference polyestercarbonate. This effect is illustrated in Figure 5. The results showed that with all other parameters essentially unchanged, the increase in the stiff segment length leads to an increase in chain entanglement, improvements in impact resistance and resistance to embrittlement at low temperatures and on thermal aging. Since this modification involves an increase in Tg, there is a limitation in the length of "L" because melt processability is required. Nevertheless, the studies with the reference polyestercarbonate clearly demonstrated the improvements resulting from increases in "L" above the value in polycarbonate. Furthermore, it was shown that the reduction of carbonate linkages by a factor of two had little detrimental effect on such mechanical properties as ductility and impact resistance.


BPA-CARBONATE LEXAN

POLYESTER CARBONATE

FIGURE 5. Structures of Polycarbonate and Polyestercarbonate: Comparison of Stiff Segment Length

Using the concepts developed for the properties of bisphenol-A polycarbonate and the polyestercarbonate, the molecular design of suitable candidates (i.e., higher Tg) for high performance windshield/canopy materials can be met with the following criteria:

1. Tg in the range of 200-250°C for melt processability.
2. Chain interaction similar to BPA polycarbonate and the reference polymer.
3. Stiff segment length "L" greater than that of BPA polycarbonate but in the same range as that for the reference polymer.
4. Absence of carbonate moities or at least sufficient reduction to maintain Tg.

By employing the Van Krevelen approach of calculating the Tg of amorphous polymers by manipulation of the monomeric components, the above requirements could be met at least in principle by using various diacids in combination with BPA. With this approach it was possible a priori to optimize stiff segment length, chain interaction and Tg.

The most promising result of this approach was the polyester composed of bisphenol-A and 4,4'-benzophenone dicarboxylic acid (BDA). The Van Krevelen calculation indicated that this material would have a Tg of 205°C. The structure which is displayed in Figure 6 has structural similarity to the reference material as well as similarity in the average stiff segment length. Yet there exists enough flexibility in the ketone carbonyl groups (R) to permit greater melt processability than for example in the corresponding terephthalate or 4,4'-biphenyl polyesters of BPA.

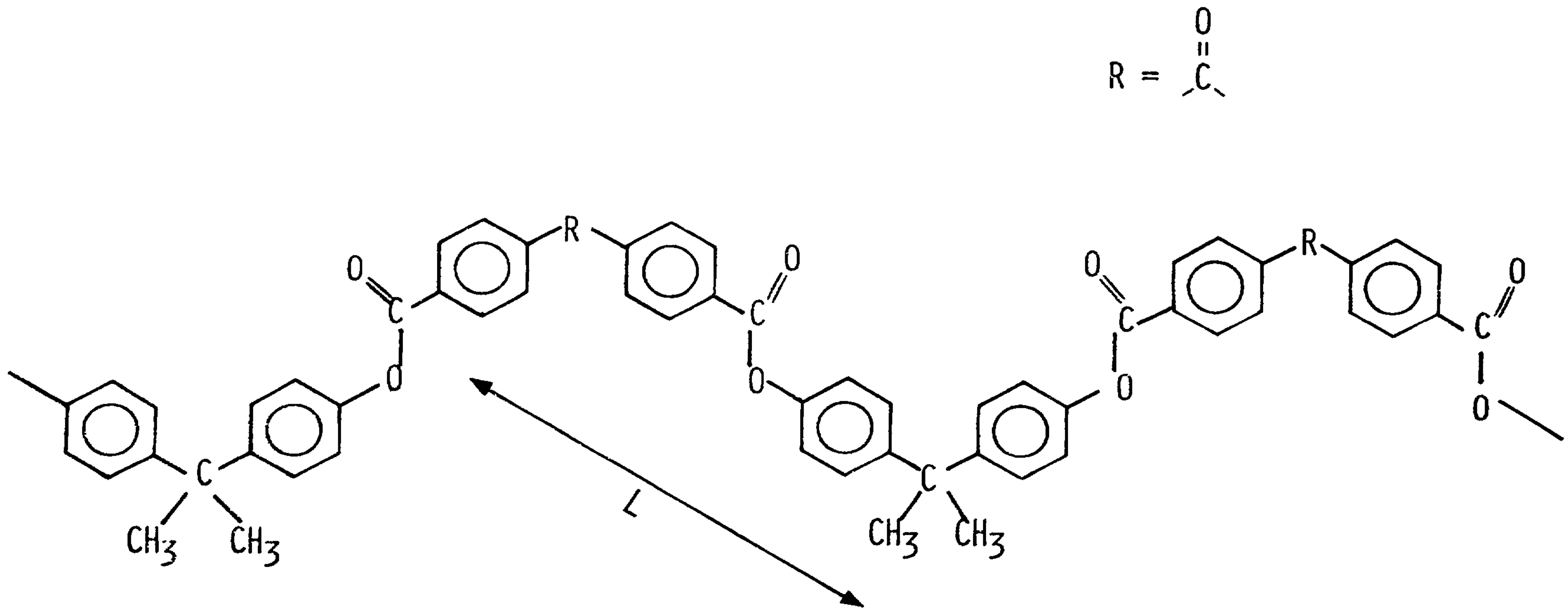
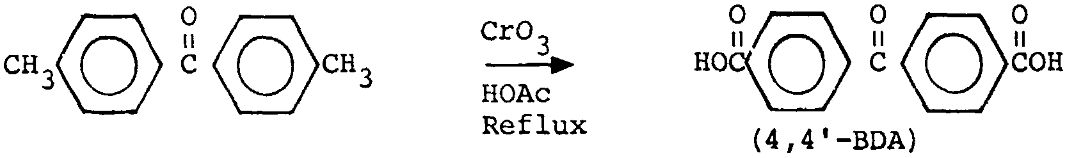


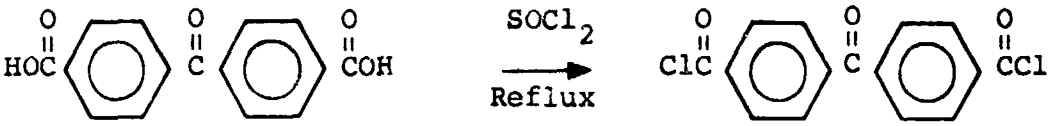
FIGURE 6. Polyester of BPA and 4,4'-Benzophenone Dicarboxylic Acid

3.2.1 Synthesis of 4,4'-Benzophenone Dicarboxylic Acid Chloride (BDAC)

In order to directly prepare polyesters containing the 4,4'-benzophenone dicarboxylate unit, suitable methods had to be identified at least for the preparation of the corresponding dicarboxylic acid (BDA). The approach chosen to obtain this compound was the oxidation of 4,4'-dimethylbenzophenone by chromium trioxide in acetic acid.



The diacid could be obtained in a pure form only after difficult purification steps involving the diammonium salt. From the diacid several approaches were available for conversion to high molecular weight polyesters with aromatic diols. The first considered was melt transesterification. However, this approach was eliminated for the purposes of this program by virtue of the likelihood of color formation during the melt polycondensation process. Among the mildest approaches available was low temperature polycondensation through the acid chloride. Thus, the 4,4'-BDA was converted to the diacid chloride by means of thionyl chloride.



(4,4'-BDAC)

This compound after suitable purification was employed in the synthesis of all corresponding polyesters.

3.2.2 Polyester of BPA and 4,4'-BDAC - AF-TP-9 Series

For the preparation of the polyester derived from BPA and 4,4'-BDAC (AF-TP-9) both solution and interfacial polymerization techniques were studied in order that the most effective method could be chosen for obtaining material of sufficiently high molecular weight and purity. In small scale experiments solution techniques (inert solvent and pyridine acid acceptor) gave materials of only moderate molecular weight at best. The highest solution viscosity for preparations conducted in homogeneous solution was obtained with chloroform as the reaction solvent. Preparations conducted in dichloromethane gave somewhat lower values of solution viscosity, but in either case the molecular weights were judged to be too low for the program applications. On the other hand with interfacial techniques in the presence of benzyl triethyl ammonium chloride as a reaction catalyst, acceptably high molecular weights were achieved especially with chloroform as the polymer phase solvent. Some typical results for small scale experiments are presented in Table 7.

TABLE 7. POLYESTER DERIVED FROM BPA AND 4,4'-BDAC (AF-TP-9)

Entry	Process[a]	Reaction Solvent	η_{sp}/C (dl/g)[b]	Tg (°C)
1	Solution	CH_2Cl_2	0.39	180
2	Solution	CH_2Cl_2	0.41	180
3	Solution	CH_2Cl_2	0.42	180
4	Solution	$CHCl_3$	0.56	200
5	Solution	$CHCl_3$	0.58	200
6	Interfacial	CH_2Cl_2	0.81	210
7	Interfacial	$CHCl_3$	1.21	210

a. 1:1 mole ratio BPA: 4,4'-BDAC in all cases

b. C = 0.5 in phenol/TCE at 25°C

For the highest molecular weight sample prepared, the measured Tg value corresponded quite well with the calculated value. In order to obtain sufficient polymer for characterization and testing the best procedures (i.e., entries 6 and 7 of Table 7) were chosen for further work involving laboratory scale-up.

Although the first larger scale AF-TP-9 preparation (100 g) had a reasonable solution viscosity (0.81 dl/g), the color of a 1/8" thick disc compression molded at 320°C was much too dark for the considered application. Attempts to reduce the color by use of lower molding temperatures were generally unsuccessful. Considerable attention was directed toward color reduction by improved acid chloride purification measures. Some limited success was achieved by careful decolorization of the crude acid chloride followed by repeated recrystallization from toluene.

In all cases AF-TP-9 preparations were identical with respect to IR and NMR spectra. The primary batch-to-batch differences were in the molecular weights as reflected by solution viscosity values. Solvent cast films of AF-TP-9 were transparent and unusually tough as observed by a high degree of tear and flex-cracking resistance. Although the tensile properties were similar to those of AF-TP-2, the notched IZOD impact values were exceptionally good especially in consideration of the high Tg of the material. Typical IZOD values of 5 ft-lb/in at 25°C were obtained for materials having $\eta_{sp}/C > 0.8$. This result was both surprising and most encouraging, since it demonstrates that this new polyester remains ductile at least down to 190°C below its Tg. A few selected properties of AF-TP-9 are displayed in Table 8.

TABLE 8. SELECTED PROPERTIES OF AF-TP-9

Tensile Elongation	15.5%
Ultimate Tensile Strength	10,600 psi
Tensile Modulus	288,000 psi
Notched IZOD Impact	~5 ft-lb/in
Heat Distortion Temperature	190°C @ 264 psi
Tg	210°C

3.2.3 Other Polyesters Derived from 4,4'-BDAC

The encouraging tensile, impact and thermal properties of AF-TP-9 led to the investigation of other BDA polyesters based on aromatic diols. The two materials which were investigated were the corresponding polyesters of DCB and TMDCB. In general the same difficulties were encountered in the synthesis as with the BPA polyester. However, with these two monomers high molecular weights were not achievable even by the interfacial method involving catalysis with quaternary ammonium salts. Thus, in this respect the resultant polymers were not particularly advantageous to the program, since theoretically possible Tg's could not be realized. In addition these two polyesters showed no improvement in color after molding over that of AF-TP-9. Viscosity and thermal data for these two polyesters are shown in Table 9.

TABLE 9. POLYESTERS OF 4,4'-BDAC AND DICUMYLBISPHENOLS

Entry	Aromatic Diol	Process	η_{sp}/C (dl/g)	Tg (°C)
AF-TP-9A	DCB	IF[a]	0.13	150(?)
AF-TP-9A-1	DCB	IF[b]	0.52	190
AF-TP-9B	TMDCB	IF[b]	0.50	206

a. Polymer phase solvent CH_2Cl_2

b. Polymer phase solvent $CHCl_3$

Without doubt the molecular weights of the above polyesters could be raised by judicious changes in such reaction variables as temperature, polymer phase solvent, catalyst type as well as concentration and stirrer speed. However, at this time it was felt that efforts should be concentrated on the further evaluation of the BPA polyester.

4.0 RESULTS

4.1 Thermal and Optical Properties

4.1.1 Polycarbonates

Thermal stability and optical properties of the prepared materials which are classed as polycarbonates are displayed in Table 10. For this work both the glass transition temperature (Tg, by DSC) and the onset of weight loss (TGA) were taken as an indication of the usefulness of the materials in terms of thermal dimensional stability and thermal decomposition. In all cases the Tg and TGA measurements were conducted in an argon atmosphere under conditions considered typical for exploratory polymer research (see Section 7.5, Polymer Characterization and Evaluation). Indicated TGA values are the approximate temperatures at which the accelerated decomposition rates are maximum. Optical properties were determined on 1/8" thick discs which were compression molded under specific conditions. For purposes of comparison typical literature values for BPA polycarbonate (Lexan®) have been included.

TABLE 10. THERMAL AND OPTICAL PROPERTIES OF POLYCARBONATES

			Thermal		Optical*		
Polymer	Monomer	η_{sp}/C (dl/g)	Tg (°C)	TGA (°C)	%T	%H	YI
AF-TP-1B	TMBA	0.87	195	400	ND	ND	ND
AF-TP-1B-1	TMBA	1.23	200	400	83[a]	10	8
AF-TP-2A	TMDCB	1.93	190	400	ND	ND	ND
AF-TP-8	DCB	1.80	156	400	84[b]	7	7
Lexan®	BPA	0.7-1.2	150	400	86-89	1-2	2

* %T = % Transmittance
%H = % Haze
YI = Yellowness Index

a. Molded at 320°C
b. Molded at 290°C
ND = not determined

Of the above polycarbonates only AF-TP-1B-1 which is a higher molecular weight version of AF-TP-1B meets the Tg objective of $\geq$ 200°C. The optical values obtained for this material are reasonably good considering that no special precautions were made to eliminate dust in the preparation and handling of the polymer. Also no stabilizers or tinting agents were employed in this study. Unless needed for reference purposes the optical values were not determined in cases where the Tg did not meet the target objective.

4.1.2 Polyesters

Thermal and optical values for the various polyesters prepared are shown in Table 11. The majority of the materials are either terephthalates or 4, 4' - benzophenone dicarboxylates of aromatic diols.

TABLE 11. THERMAL AND OPTICAL PROPERTIES OF POLYESTERS

Polymer	Monomers		η_{sp}/C (dl/g)	Thermal		Optical		
	Diol	Diacid		Tg (°C)	TGA (°C)	%T	%H	YI
AF-TP-1	TMBA	Oxalic	4.00	153	350	ND	ND	ND
AF-TP-1A	TMBA	Terephthalic	1.90	253	400	70	35	24
AF-TP-2B	TMDCB	Terephthalic	1.01	228	350	82	28	14
AF-TP-7	TMDCB	Terephthalic/ Isophthalic (1:1)	0.98	212	400	81	31	22
AF-TP-8A	DCB	Terephthalic	insol.	ND	ND	ND	ND	ND
AF-TP-9	BPA	4,4'-BDA	0.81	200	400	ND	ND	very dark
AF-TP-9-1	BPA	4,4'-BDA	0.42	180	350	ND	ND	very dark
AF-TP-9-2	BPA	4,4'-BDA	1.13	210	400	71	20	90
AF-TP-9A	DCB	4,4'-BDA	0.13	150 (?)	ND	ND	ND	ND
AF-TP-9A-1	DCB	4,4'-BDA	0.52	190	400	76	23	>100
AF-TP-9B	TMDCB	4,4'-BDA	0.50	206	400	80	28	93
U-Polymer*			0.6-0.8	185	-	67	20	64

a. All molded at 320°C

* Unitika - Union Carbide polyester of BPA and Tere-isophthalic acid blend.

In spite of acceptable Tg values, all terephthalates and the one example of a tere-isophthalate blend showed a distinct tendency to crystallize upon thermal treatment. In most cases the crystallization was observed indirectly by the high haze values after compression molding which could be seen even by visual examination. In the case of AF-TP-8A extensive crystallization occurred during vacuum drying of the precipitated polymer (120°C). For this material the degree of crystallinity was so high that the material was substantially insoluble in common organic solvents. The oxalate polyester of TMBA in addition to having a very low Tg was unstable at 25°C in the presence of air with a relative humidity of 25-80%. All polyesters derived from 4, 4'-BDA had high yellowness index values, although by visual matching 9-2 and 9B were close in color to polysulfone and about equal to U-polymer.

4.1.3 Polyestercarbonates

The thermal and optical values for polyestercarbonate copolymers are shown in Table 12 together with the corresponding values for the reference polyestercarbonate. With the exception of 2C, 6-1, 6-2 and 6-3, the polyestercarbonate copolymers come close to both the thermal and optical objectives for this program. Although haze and color values are higher than desirable, it should be kept in mind that these values were obtained on laboratory samples which were not subjected to the same rigorous precautions against contamination as the reference

TABLE 12. THERMAL AND OPTICAL PROPERTIES OF POLYESTERCARBONATES

Polymer	Monomers		η sp/C	Thermal		Optical[a]		
	Diol(s)	Diacids[a]		Tg (°C)	TGA (°C)	%T	%H	YI
AF-TP-1C	TMBA	TPA/Carbonate	1.43	223	400	81	15	20
AF-TP-2	TMDCB	"	1.80	210	400	80	20	23
AF-TP-2-1	"	"	0.67	207	400	80	22	19
AF-TP-2-2	"	"	4.06	214	400	82	19	15
AF-TP-2C	"	NDA/Carbonate	0.65	175	375	ND	ND	ND
AF-TP-3	90 TMDCB 10 BPA	TPA/Carbonate	1.40	210	380	ND	ND	ND
AF-TP-4	80 TMDCB 20 BPA	"	1.10	208	400	81	18	18
AF-TP-5	70 TMDCB 30 BPA	"	0.81	205	400	83	16	18
AF-TP-6	60 TMDCB 40 BPA	"	1.00	200	400	85	11	9
AF-TP-6-1	"	"	insol.	ND	ND	ND	ND	ND
AF-TP-6-2	50 TMDCB 50 BPA	"	0.80	195	400	ND	ND	ND
AF-TP-6-3	40 TMDCB 60 BPA	"	0.91	191	400	ND	ND	ND
Polyestercarbonate*			0.70	182	400	83-90	2-5	3-8

a. 1:1 mole ratio in feed and final copolymer.
b. All molded at 320°C, 1/8" thick discs.
* Allied Chemical Corp. BPA terephthalate - carbonate copolymer.

polyestercarbonate. Such measures as removal of all dust and foreign particles by pressure filtration of polymer solutions would be expected to improve the haze values considerably. Color improvement could be expected by minimizing exposure to air during compression molding.

4.1.4 Heat Deflection Temperature Measurements

For the most promising candidates comprising the three classes of polymers prepared, heat deflection temperatures (HDT) were measured and compared to the corresponding Tg values obtained by DSC. For the considered application it was felt that HDT values would be somewhat more meaningful than the Tg's alone. The values for the selected polymers are displayed in Table 13, along with typical reference materials. In all cases the HDT is between 10-20°C lower than Tg, as expected.

TABLE 13. HEAT DEFLECTION TEMPERATURE VALUES FOR SELECTED POLYMERS

Polymer	Tg (°C)[a]	HDT (°C)[b]
AF-TP-2	210	190
AF-TP-2-1	207	189
AF-TP-2-2	214	194
AF-TP-6	200	186
AF-TP-9	200	190
AF-TP-9-2	210	193
Polyestercarbonate	182	165-175
U-Polymer	185	175
Polysulfone (UDEL®)	188	168
BPA Polycarbonate (Lexan®)	150	140

a. by DSC, see Section 7.5, Polymer Characterization and Evaluation
b. 264 psi, see Section 7.5, Polymer Characterization and Evaluation

4.2 Mechanical Properties

At this stage in the program a preliminary evaluation of mechanical properties was undertaken to include only those materials which met the Tg objective and showed sufficently good optical properties to qualify as "transparent" plastics. The mechanical properties evaluation involved the determination of tensile properties such as yield elongation, yield strength, ultimate elongation, ultimate tensile strength and tensile modulus employing ASTM Type V specimens of 1/32" thickness. Izod impact strength was evaluated in most cases using the standard 1/8" specimen in the notched configuration. In some selected cases reverse or unnotched configuration was employed. The data obtained up to this point are displayed in Table 14. Polymer sample 1C shows tensile behavior typical of brittle materials. Thin molded sheets of this material (1/32") could not be flexed more than 30° by hand without breaking. Thus, Izod impact values were not determined for this polyester or others of the same class which were obviously brittle. With the exceptions of UE values, the tensile properties of materials 2 through 9 in the table are similar to those of the three materials included as controls. For the AF-TP-2 series (2 through 2-2), the best overall tensile properties seem to be for the sample of highest molecular weight, AF-TP-2-2. The fact that good tensile properties do not necessarily correlate with good notched impact performance can be seen from the Izod impact values. Thus,

TABLE 14. PRELIMINARY MECHANICAL PROPERTIES OF SELECTED POLYMERS

Polymer	Tg (°C)	YE(%)	YS (PSI)	UE(%)	UTS (PSI)	TM (PSI X10^3)	IZOD Impact (ft-lb/in) 1/8" Notched	IZOD Impact (ft-lb/in) 1/8" Unnotched
AF-TP-1C	223	b	b	7.4	6690	295	ND[c]	ND[c]
AF-TP-2	210	16.1	10630	50	9120	306	1.0	22
AF-TP-2-1	207	17	9980	80	9160	264	1.0	20
AF-TP-2-2	214	18.1	10100	90	9180	284	1.2	24
AF-TP-2A	190	14.5	-	18.7	11300	326	1.0	ND
AF-TP-2B	228	19.5	10740	33	-	272	ND	ND
AF-TP-6	200	25	10000	80	9500	275	2.0	26
AF-TP-7	212	21	9653	41	9200	243	ND	ND
AF-TP-9	200	15.5	-	-	10600	288	5.5	ND
AF-TP-9-2	210	19	9920	27	10400	307	5.0	28
Polyestercarbonate*	182	18.3	9100	70	9600	266	5-8	31
BPA Polycarbonate* (Lexan®)	150	12.8	8810	120	9540	297	12-16	ND
Polysulfone* (UDEL®)	188	11	10100	90	9100	320	1.3	ND

a. ASTM Type V, 1/32", average of at least 8 specimens
b. All specimens broke before yield
c. Not determined because material too brittle
* Determined on ASTM Type V specimens

AF-TP-9-2 which has a somewhat low value for UE has a rather high Izod value. In contrast AF-TP-2-2 has a value for UE approaching that of BPA polycarbonate but an impact resistance one order of magnitude lower. The same behavior can be seen with polysulfone.

For several cases in which the notched impact resistance was low, unnotched impact was evaluated primarily to provide an indication of the sensitivity of materials to imperfections such as scratches. The AF-TP-2 series shows a high degree of notch sensitivity especially in comparison to the reference polyester-carbonate.

The replacement of 40 mole % of the TMDCB monomer in AF-TP-2 by BPA gives the copolymer AF-TP-6. The effect of this modification results in an increase in YE as well as a substantial improvement in the notched Izod performance. Even greater improvement in the impact performance could be expected at higher levels of BPA with respect to TMDCB in the copolymers. However, an examination of Tg values for such copolymers (AF-TP-6-2 and 6-3) in Table 12 indicates that the practical limit of BPA in such copolymers is about 40 mole % in terms of a minimum Tg objective of 200°C.

For many thermoplastic materials it has been observed that the notched Izod impact strength depends to some extent on the preparation of the molded test piece as well as the purity of the polymer - especially the presence of oligomers. The molded sheets employed for tensile measurements and the Izod test bars for all materials in Table 14 were prepared at 320°C. It was possible that this temperature was not optimum for AF-TP-2 series and AF-TP-6. Tests were conducted to evaluate the effect of molding temperature on notched Izod impact strength using AF-TP-2 prepared by the combination solution - interfacial polycondensation method. Two materials were prepared with approximately the same molecular weights. The compression molding temperatures were varied beween 270-350°C. Also of concern was the rate of cooling after molding. However, this variable could not be controlled as well as the molding temperature. The results are shown in Table 15. In all cases there was no significant polymer degradation as evidenced by the close agreement in solution viscosity data before and after molding. With both polymers molding temperatures below about 300°C gave poorer impact properties than the higher temperatures. This result was not surprising. Although the sample molded at 270°C was completely fused by visual examination, particle boundaries could be observed under the microscope. Such boundaries act as local stress concentrators and are probably the major contributor to the slightly higher notch sensitivity observed. In the case of the one sample which was quenched, severe cracking occurred in the mold as the polymer contracted. Only those portions of the sheet which were free of visible cracks were used for measurements; however, there were no assurances that micro-cracks were not present in the test specimens. A slower cooling rate

TABLE 15. IZOD IMPACT STRENGTH OF AF-TP-2 AS A FUNCTION OF MOLDING TEMPERATURE

Polymer	η_{sp}/C (dl/g)		Molding Temp (°C)	Cooling Time[a] (min.)	IZOD Impact (ft-lb/in)[c]	
	Before Molding	After Molding			Notched	Unnotched
AF-TP-2-3	0.98	0.98	270	20	0.7	20
"	0.98	0.96	290	20	1.0	21
"	0.98	0.96	300	20	1.0	21
"	0.98	0.93	320	20	1.0	21.7
"	0.98	0.91	320	quenched[b]	0.8	20
"	0.98	0.94	320	180	1.2	22
"	0.98	0.89	350	20	1.0	21
AF-TP-2-4	1.15	1.15	290	20	0.9	20
"	1.15	1.10	320	20	1.2	22
"	1.15	0.97	350	20	1.0	22

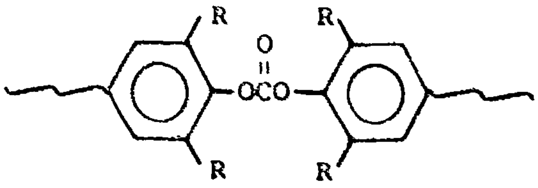
a. Time to reach 80°C mold temperature
b. Mold placed in ice-water
c. Average of 12 samples each

seemed to have only a slightly positive effect and was not pursued further at this time. No advantage was gained at high molding temperatures. With polymers containing no thermal stabilizer the use of molding temperatures greater than 350°C results in considerable chain degradation and concominant loss in mechanical properties.

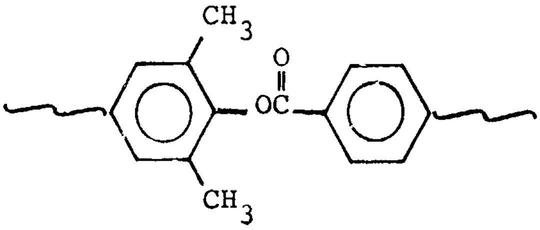
4.3 Chemical Properties

4.3.1 Hydrolysis Resistance of AF-TP-2

One secondary objective of this program has been the design of polymer systems which have improved hydrolytic stability in addition to acceptable thermal, optical and mechanical properties. For polyestercarbonate systems it was reasoned that one way of reducing the sensitivity of aromatic carbonate and ester linkages to hydrolysis, while at the same time increasing the Tg, would be to shield these linkages by means of "bulky" substituents in the ortho positions.



It was felt that the carbonate linkage in the above structure would be comparatively less accessible to hydrolyzing agents if "R" were alkyl groups such as methyl. Of course, in the polyestercarbonates covered in this work there are two types of ester linkages, carbonate and terephthalate. The carbonate ester is generally considered to be more sensitive toward hydrolysis than the ester. Thus, in the case of polyestercarbonates derived from monomer TMDCB, TPC and phosgene, the carbonate ester as shown in the above structure is highly shielded while the terephthalate ester is only partially shielded.



Relative to the carbonate ester the above partially shielded ester should still display enhanced stability as a result of its inherently greater stability.

In order to assess the hydrolytic stability of the polymers under realistic service conditions, experiments were conducted on compression molded sheets (320°C). In terms of actual data, sheet thickness was kept reasonably constant (0.4 mm) so that the weight loss per unit area values could be directly compared. Two sets of data are reported here which represent severe conditions for aqueous acid and base hydrolysis. The results of aqueous acid hydrolysis for some selected polymers are shown in Table 16.

TABLE 16. HYDROLYSIS RESISTANCE OF MOLDED POLYMER SHEETS IN HOT AQUEOUS ACID*

Polymer	Exposure Time (hrs.)	Wt. Loss (mg/cm^2)	ηsp/C (dl/g) Inital	ηsp/C (dl/g) Final
AF-TP-2	60	0	1.10	0.91
AF-TP-4	60	0	0.91	0.78
AF-TP-5	60	0	0.78	0.60
Polyestercarbonate	60	0	0.42	0.28
BPA Polycarbonate (Lexan®)	60	0	0.61	0.51

*5N HCl at 108°C

In these experiments the polymer sheets were immersed in refluxing 5N aqueous HCl for the specified times. The last two entries in the table are for reference purposes. In all cases, there was no detectable weight loss. However, the sample of polyestercarbonate showed a tendency to embrittle during the exposure and eventually broke apart. All other samples retained their original appearance and flexibility. It is interesting that AF-TP-4 and 5 which contain 20 and 30 mole % BPA in place of TMDCB respectively, do not degrade significantly or undergo embrittlement.

The results for aqueous base hydrolysis for the same sample types are shown in Table 17.

TABLE 17. HYDROLYSIS RESISTANCE OF MOLDED POLYMER SHEETS IN HOT AQUEOUS BASE*

Polymer	Exposure Time (hrs.)	Wt. Loss (mg/cm^2)	$\eta sp/C$ (dl/g) Inital	$\eta sp/C$ (dl/g) Final
AF-TP-2	60	0	1.10	0.95
AF-TP-4	60	0	0.91	0.80
AF-TP-5	60	0	0.78	0.63
Polyestercarbonate	44	4.03	0.42	-
Polyestercarbonate	60	completely degraded	0.42	-
BPA Polycarbonate (Lexan®)	<20	completely degraded	0.61	-

*5N NaOH at 80°C

It should be noted that these conditions of base concentration and temperature are extremely severe for typical polycarbonates and polyesters, as can be seen from the results for the reference materials. Both reference samples were totally degraded after 60 hours of exposure (degraded to monomers). With respect to weight loss and physical appearance, all polymers derived from TMDCB were unaffected. What is most surprising is that even co-polyestercarbonates of TMDCB containing up to 30 mole % BPA remained unaffected under these conditions. From the viscosity data in the table, it can be seen that the AF-TP samples do not show any great degree of chain scission. Results for AF-TP-6 and 9 have not been obtained at this time.

4.3.2 Solvent Resistance of AF-TP-9

Although amounts of this polyester prepared at this time have been small, some qualitative solvent resistance information has been obtained. Table 18 presents solvent resistance data in the form of weight change upon solvent immersion. Samples of the AF-TP-9 polyester were molded into 30 mil films and annealed at 220°C for 4 hours. One gram samples were immersed for 24 hours in the solvent at 23°C and the change in weight measured. The largest change in weight resulted with acetone: a 2.9% gain in weight.

TABLE 18. SOLVENT RESISTANCE OF AF-TP-9

Solvent	Change in Weight (%)
heptane	- 0.11
isopropanol	- 0.31
carbon tetrachloride	+ 0.34
toluene	+ 0.34
butyl acetate	+ 0.15
acetone	+ 2.95

Similar solvent resistance experiments are presently being conducted on AF-TP-2 and 6.

5.0 CONCLUSIONS

By comparison of thermal, optical, mechanical and chemical properties described and tabulated in Sections 4.1 to 4.3, three types of polymer systems emerge as candidates for more detailed evaluation. These materials are groups AF-TP-2, AF-TP-6 and AF-TP-9, two of which include two or more variations in molecular weight. Some of the more important characteristics are reviewed in Table 19.

TABLE 19. PROPERTIES OF CANDIDATE MATERIALS

		Thermal		Optical			Mechanical[b]		Chemical[c]	
Polymer	η_{sp}/C	Tg (°C)	HDT (°C)[a]	%T	%H	YI	IZOD(N)	IZOD(UN)	Solvent	Hydrolysis
AF-TP-2	1.80	210	190	80	20	23	1	22	ND	Superior
AF-TP-2-1	0.67	207	189	80	22	19	1	20	ND	Superior
AF-TP-2-2	4.06	214	194	82	19	15	1.2	24	ND	Superior
AF-TP-6	1.00	200	186	85	11	9	2.0	26	ND	ND
AF-TP-9	0.81	200	190	ND	ND	ND	5.5	ND	Good	ND
AF-TP-9-2	1.13	210	193	41	20	90	5.0	28	Good	ND

a. refer to Table 13
b. refer to Table 14
c. refer to Tables 16, 17, 18

The objectives of thermal stability (heat deflection) are satisfied by all three materials. With AF-TP-6 as with the others some modest increase in the Tg (and HDT) can be expected by raising the molecular weight. In all cases the materials are stable to process conditions required for fabrication, such as melt extrusion or compression molding even in the absence of thermal stabilizers.

Although good optical values were obtained for AF-TP-6, better values should be possible with this material and the AF-TP-2 series. With more rigorous purification of monomers, removal of dust and foreign particles from polymer solutions and use of stabilizers, the three optical values should improve to the point of %T >85, %H and YI <5. Optical values, especially the color, of AF-TP-9 are at this time unsatisfactory. However, improvement in the color of this polymer should be possible by more elaborate purification of the starting 4,4'-BDA as well as the use of stabilizers. It is presently felt that the majority of the color formed during molding of AF-TP-9 results from trace amounts of chromium salts carried over in the monomer after synthesis.

Although the tensile properties of the AF-TP-2 series appear to be satisfactory, the notched IZOD impact resistance is considerably lower than desired. Other than secondary chemical modifications to AF-TP-2 materials, there seems to be at this time no way to improve the notched impact performance beyond about 1.2 ft-lb/in. The notched IZOD impact resistance of

AF-TP-6 is considered to be borderline, and only marginal improvement can be expected from modifications such as an increase in molecular weight or changes in molding conditions. Both materials may continue as candidates if shown to be superior in other characteristics after more detailed testing. AF-TP-9 without question has satisfactory mechanical properties - especially impact strength - to warrant further study.

From the hydrolysis resistance experiments it is clear that all materials containing significant amouunts of TMDCB monomer (i.e. AF-TP-2, 6) have superior stability to strong mineral acids and base with respect to both chain scission and embrittlement. AF-TP-9 by virture of having a high aromatic ester content is quite solvent resistant. However, solvent crazing experiments must be undertaken for all materials in the table before meaningful conclusions can be drawn.

6.0 RECOMMENDATIONS

Research efforts are continuing along two main areas. Exploratory work is being carried out on identifying other structures which are capable of raising the Tg of the reference polyestercarbonate, and more detailed testing of the existing candidates along with improvements in their deficiencies where possible is in progress.

As a result of the findings presented in this report, other monomer structures have been identified which at levels as low as 10 to 30 mole % replacement of BPA give rise to increases in the Tg of polyestercarbonates well over those of AF-TP-2, 6 and 9. Although this phase of the research is still in the exploratory stages, it is expected that materials having excellent mechanical and optical properties will be possible as the result of less overall perturbation of the basic polyestercarbonate structure.

Laboratory scale up efforts are planned for candidate materials AF-TP-2, 6 and 9 so that sufficient polymer will be available for the evaluation of such properties as Taber abrasion, solvent, ultraviolet light, weathering and thermal aging resistance. In addition, efforts are being made to improve the optical properties of these materials by the methods described in this report.

The results for both areas of research will be reported on in the upcoming monthly and quarterly reports.

7.0 EXPERIMENTAL

7.1 Preparation of Intermediates and Monomers

7.1.1 o,o,o',o'-Tetramethylbisphenol A (TMBA)

A solution of 2,6-dimethyl phenol (122.16 g, 1 mole) in anhydrous acetone (58.08 g, 1 mole) was saturated with anhydrous HCl gas at room temperature until a constant weight was achieved. The solution was allowed to stand at room temperature for 48 hours, during which time crystallization occurred. The solid product was crushed, washed repeatedly with water and dried. The solid was then dissolved in methanol (1 l) and decolorized with animal charcoal. The resultant soluton was concentrated to ca. 550 ml, diluted while hot with 120 ml water, and set aside to crystallize. The light amber crystals were filtered and dried, yield = 100 g (70%), mp = 164-168°C. The product was further purified by recrystallization three times from 200 ml toluene. Final yield = 90 g, mp 168-169°C. The NMR spectrum ($CDCl_3$) at 60 MHz showed a singlet at 1.58 δ (aliphatic gem-CH_3), a singlet at 2.17 δ (aromatic CH_3) and a singlet at 6.82 δ (aromatic protons) in a ratio of 6:12:4. Elem. anal. calcd ($C_{19}H_{24}O_2$) %C = 80.24, %H = 8.51; found %C = 80.18, %H = 8.38.

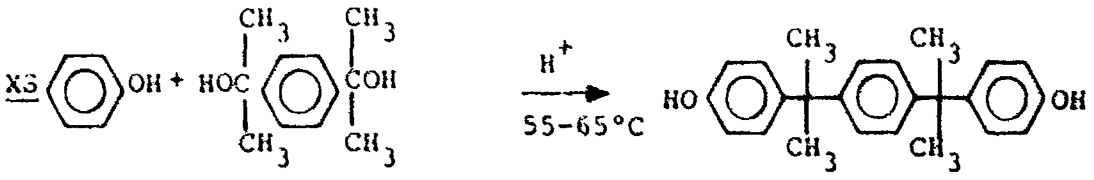
7.1.2 p-Diisopropylbenzene-α,α'-Diol

The intermediate diol was prepared by oxidation of p-diisopropylbenzene.

Gaseous oxygen was bubbled into a vigorously stirred suspension of the hydrocarbon (900 g) in 40% aqueous sodium hydroxide (1260 g) at 100°C for 10 hours. The crude product was filtered, extracted with petroleum ether and then water until neutral. The product was recrystallized from ethanol/water to give 294 g of material which was further purified by two recrystallizations from 1,2-dichloroethane. The final yield of highly pure diol was 255 g with mp = 142-144°C. Elem. anal. calcd ($C_{12}H_{18}O_2$) %C = 74.19, %H = 9.34; found %C = 74.28, %H = 9.44. The 60 MHz NMR spectrum ($CDCl_3$/DMSO-D_6) showed a singlet at 1.5 δ (aliphatic gem-CH_3), a broad singlet at 4.4 δ (OH) and a singlet at 7.4 δ (phenyl) with an integration ratio of 12:2:4 as required by the proposed structure. Unreacted diisopropylbenzene extracted in the petroleum ether was recycled in subsequent preparations.

7.1.3 Dicumylbisphenol (DCB)

This monomer was prepared by the acid catalyzed condensation of phenol with the above diol.



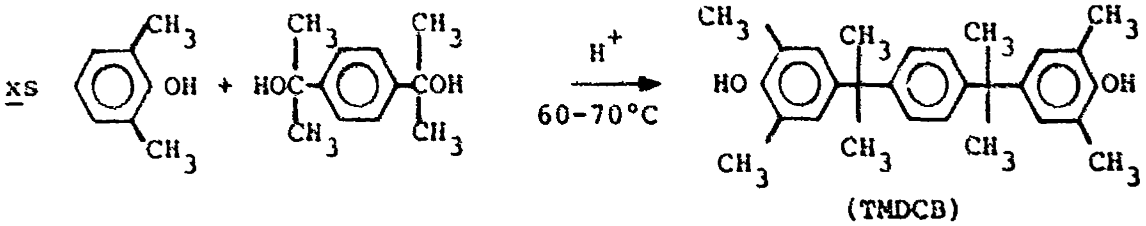
(DCB)

The purified α,α'-diol (97.2 g, 0.5 mole) was added in 10 g portions over a period of two hours to a soluton of p-toluenesulfonic acid (2.5 g, 0.015 mole) in reagent grade phenol

(470.5 g, 5 moles) at 55-60°C. After the addition the solution was heated with stirring at 65°C for two hours. Water was added to about five times the volume of reaction product and the mixture was subjected to steam distillation to remove unreacted phenol. The white solid residue was collected by filtration, washed with water and dried at room temperature. The crude yield was 174 g (quantitative). The product was recrystallized once from a mixture of 348 ml methanol and 86 ml water with cooling to 10-15°C (recovery = 116.5 g). A second recrystallization was done with 233 ml methanol and 60 ml water and gave 103.5 g of pure material with mp = 168-170°C. Elem. anal. calcd ($C_{24}H_{26}O_2$) %C = 83.20, %H = 7.56; found %C = 83.16, %H = 7.63. The 60 MHz NMR spectrum ($CDCl_3/DMSO-D_6$) showed a singlet at 1.60 δ (aliphatic gem-CH_3), an AA'BB' pattern centered at 6.90 δ (phenolic ring protons), a singlet at 7.10 δ (phenyl ring protons) overlapped and a broad singlet at 10.3 δ (OH). The integration ratio was 12:12:2 as required by the structure.

7.1.4 o,o,o',o'-Tetramethyldicumylbisphenol (TMDCB)

This monomer was prepared by acid catalyzed condensation of 2,6-dimethylphenol with the α,α'-diol.



Purified α,α'-diol (109 g, 0.56 mole) was added in 10 g portions over two hours to a solution of p-toluene sulfonic acid (2.8 g, 0.17 mole) in freshly distilled 2,6-dimethyl phenol (686 g, 5.6 moles) at 65°C. After addition was completed, the solution was stirred at 65-70°C for an additional 2 hours. Water was then added to about five times the volume and the catalyst neutralized with aqueous ammonia. The mixture was subjected to steam distillation until the removal of unreacted phenol was complete. The yield of crude solid at this point was 212 g (94% based on diol). The solid was dissolved in chloroform (940 ml) and the solution decolorized with animal charcoal and filtered. The solvent was evaporated to dryness on a rotoevaporator. The solid was recrystallized twice from cyclohexane to give 128 g of pure white crystalline monomer, mp = 158-160°C. Elem. anal. calcd ($C_{28}H_{34}O_2$) %C 83.54, %H = 8.51; found %C = 83.77, %H = 8.46. The 60 MHz NMR spectrum ($CDCl_3$/DMSO-D_6) showed a singlet at 1.53 δ (aliphatic gem-CH_3), a singlet at 2.16 δ (aromatic CH_3), a broad singlet at 5.56 δ (OH), a singlet at 6.78 δ (aromatic protons on phenolic ring) and a singlet at 7.08 δ (aromatic protons on phenyl ring. The integration ratio was 12:12:2:4:4 as required by the proposed structure.

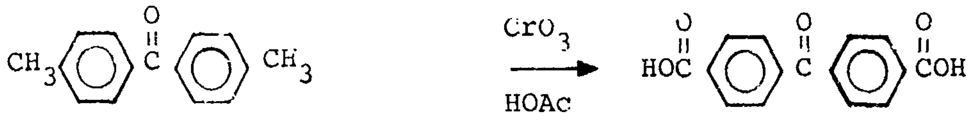
7.1.5 2,6-Naphthalene Dicarboxylic Acid Chloride (NDAC)

The dimethyl ester of 2,6-naphthalene dicarboxylic acid (50 g, 0.3 mole) was hydrolyzed to the diacid salt by refluxing in a solution of sodium hydroxide (50 g, 1.25 moles) in water (800 ml) until no more solid diester remained. The salt solution was then neutralized with dilute aqueous sulfuric acid to precipitate the free diacid. The crude product was collected by filtration and dried in a vacuum oven at 80°C. The crude yield was 43.1 g (98%). Elem. anal. calcd ($C_{12}H_8O_4$) %C = 66.67, %H = 3.70; found %C = 66.91, %H = 4.01.

The above diacid (43.1 g, 0.2 mole) was added to a flask equipped with a mechanical stirrer, reflux condenser and oil bath. Commercial thionyl chloride (236 g, 2 moles) containing N,N-dimethylformamide (7.3 g, 0.1 mole) was added, and the mixture was refluxed for five hours during which time the diacid gradually dissolved. The solution was then concentrated to ca. 100 ml by distillation of the excess thionyl chloride. Toluene (550 ml) was added and the final traces of thionyl chloride removed under reduced pressure along with 400 ml of toluene. The solution was allowed to cool to 0°C. After 24 hours at 0°C the crystalline diacid chloride was isolated by filtration in an inert atmosphere (argon). The yield of light yellow solid after vacuum drying at 50°C was 40 g (80%), mp = 180-184°C. Two more recrystallizations from toluene raised the mp to 182-186°C (lit. mp = 187°, Beilstein). Elem. anal. calcd ($C_{16}H_6Cl_2O_2$) %C = 56.95, %H = 2.39, %Cl= 28.02; found %C = 56.41, %H = 2.46, %Cl = 28.91.

7.1.6 4,4'-Benzophenonedicarboxylic Acid Chloride

This monomer was prepared from the corresponding 4,4'-dimethylbenzophenone by oxidation with chromium trioxide in acetic acid.



(4,4'-BDA)

To a flask equipped with mechanical stirrer, large condenser, thermometer and addition port was added 4,4'-dimethylbenzophenone (200 g, 0.95 mole), glacial acetic acid (3290 ml) and acetic anhydride (119.6 ml). With stirring, the mixture was brought to a gentle reflux by means of an electric heating mantle. Granular chromium trioxide (923 g, 9.23 mole) was then carefully added in small portions over several hours, while the mixture was maintained at gentle reflux and stirring. The mixture was refluxed for an additional 30 hours. The crude reaction product was precipitated into 5 l of water and collected by filtration on sintered glass funnels. The product was washed with sufficient water to remove all the soluble chromous salts. The wet filter cake was then dissolved in 4 l of aqueous ammonium hydroxide (2:1 water:conc. NH_4OH) at 40°C with stirring. The substantially clear solution was filtered to remove some small insoluble particles. The clear filtrate was then added to 24 l of acetone (batchwise) to precipitate the pure diammonium salt as a fine white powder. The salt was collected by filtration and dried. The dry salt was then dissolved in water (4 l) at 40°C and the resultant solution was filtered to remove a small amount of insolubles. The free pure dicarboxylic acid was isolated by acidification of the clear filtrate with dilute aqueous HCl. The white precipitated diacid was collected by filtration and dried in a vacuum oven at 100°C. The yield was 200 g (78%). Elem. anal. calcd. ($C_{15}H_{10}O_5$) %C = 66.66, %H = 3.73; found %C = 66.51, %H = 3.90. Neutralization equivalent calcd. = 135.11, found = 135.3.

To a 3 l flask equipped with a mechanical stirrer, reflux condenser, distillation adaptor and oil bath was added 4,4-benzophenone dicarboxylic acid (88 g, 0.326 mole) along with thionyl chloride (1467 ml) and N,N-dimethylformamide (2.9 ml). The mixture was refluxed for a total of seven hours with stirring during which time HCl was evolved. Toluene (220 ml) was added and the excess thionyl chloride was distilled from the mixture. When all the thionyl chloride had been removed, the volume of the residue was adjusted to about 300 ml with toluene. The clear brownish solution was rapidly filtered while hot. The acid chloride crystallized as light amber crystals as the filtrate cooled. The product was collected by filtration, dissolved in dichloromethane at reflux and decolorized with animal charcoal. The light yellow solution was then evaporated on a rotoevaporator and the residue was recrystallized from toluene to give 60 g of very light amber crystals of mp = 135-137°C. Elem. anal. calcd. ($C_{15}H_8Cl_2O_3$) %C = 58.66, %H = 2.62 %Cl = 23.09; found %C = 58.96, %H = 2.98, %Cl = 23.21. The nmr spectrum of the compound was consistent with the proposed structure.

7.1.7 Other Monomers and Intermediates

Ultra high purity bisphenol-A (Union Carbide, UHP Polycarbonate Grade) was used without further purification. Terephthaloyl and isophthaloyl chlorides were obtained from various commercial sources in the best grade available. Both were further purified of free diacids by recrystallization from heptane. Reagent grade phosgene gas was obtained from MC&B Corp. and was used without purification. Reaction solvents in all cases were purified by distillation or if necessary distillation from drying agents. All other reagents were of the best grade obtainable from commercial supply houses and were used without further treatment unless otherwise noted.

7.2 Preparation of Polymers

7.2.1 TMBA Oxalate (AF-TP-1)

A solution of TMBA (13.10 g, 0.0457 mole); anhydrous pyridine (7.74 ml. 0.0961 mole) and anhydrous dichloromethane (91.5 ml) was prepared in a flask equipped with a magnetic stirrer, dropping funnel and water bath at 5°C. To the above solution freshly distilled oxalyl chloride (6.10 g, 0.0480 mole) dissolved in dichloromethane (47 ml) was added dropwise over one-half hour with good stirring. After addition the viscous solution was stirred an additional 20 minutes and was then diluted with dichloromethane (200 ml). The polymer solution was precipitated in methanol (10:1 volume ratio) in a blender. The yield was quantitative, $\eta_{sp/c}$ = 4 dl/g (C = 0.5, phenol/TCE). Elem. anal. calcd ($C_{21}H_{22}O_4$) %C = 74.53, %H = 6.55; found %C = 74.37, %H = 6.51. The Tg of the dried polymer was 153°C (DSC). TGA (argon) showed rapid decomposition above 350°C.

7.2.2 TMBA Terephthalate (AF-TP-1A)

The solution polycondensation method described above was also employed for the preparation of the terephthalate polyester. The $\eta_{sp/c}$ values for this polyester typically ranged from 0.4 to 0.8 dl/g in phenol/TCE when pyridine alone was used as acid acceptor - catalyst. However, with small amounts of 4-N,N-dimethylaminopyridine as cocatalyst (10 mole % based on pyridine) the $\eta_{sp/c}$ values increased to about 1.0 dl/g.

It was found that higher molecular weight terephthalate could be obtained by interfacial polycondensation. A slurry of TMBA (28.44 g, 0.1 mole) in a solution of distilled water (357 ml) containing sodium hydroxide (12.0 g, 0.3 mole), benzyl triethyl ammonium chloride (0.71 g) and sodium dithionite (0.14 g) was prepared under a nitrogen atmosphere. Terephthaloyl chloride (20.30 g, 0.1 mole) dissolved in dichloromethane (350 ml) was then added over 30 minutes while the two-phase system was stirred at 300 rpm at 25°C. The resultant mixture was stirred for an additional 30 minutes during which time the viscosity increased markedly. The mixture was then acidified with acetic acid and the viscous polymer phase was separated and washed with water until neutral. The polymer was isolated by precipitation in methanol. The yield was essentially quantitative. $\eta_{sp/c}$ = 1.9 dl/g (c = 0.5, phenol/TCE). Elem. anal. calcd ($C_{27}H_{26}O_4$) %C = 78.23, %H = 6.32; found %C = 77.94, %H = 6.41. The Tg of the polymer was 253°C (DSC) with no indication of melting up to 375°C. TGA (argon) showed the start of slow weight loss at 300°C with major degradation occurring at 400°C.

7.2.3 TMBA Polycarbonate (AF-TP-1B)

TMBA (28.44 g, 0.1 mole) was added to a solution of distilled water (300 ml) containing sodium hydroxide (32 g, 0.8 mole) and triethylamine (1.4 ml, 0.01 mole) under a nitrogen atmosphere. The mixture was maintained throughout the experiment at 20-25°C and was stirred at 300 rpm after addition of dichloromethane (300 ml). Phosgene gas was then added to the vapor space of the flask at such a rate that the pH of the aqueous phase reached a value of 7 after 90 minutes. This procedure insures that all phenolic hydroxyls are converted to chloroformate ester. At this time additional sodium hydroxide (25 g, 0.635 mole) was added and stirring continued for an additional three hours. During this time the viscosity increased greatly. The mixture was diluted with 200 ml each of water and dichloromethane and acidified with acetic acid. The polymer phase was washed with water until neutral. The polymer was isolated by precipitation in methanol. The yield of dry polymer was 97%, $\eta_{sp/c}$ = 0.87

dl/g (C = 0.5 phenol/TCE). %C = 77.39, %H = 7.14; found %C = 77.51, %H = 7.23. The Tg of the polymer was 195°C (DSC) with no indication of melting up to 285°C TGA (argon) indicated thermal stability up to about 300°C with major decomposition occurring above 400°C.

A higher molecular weight version (1B-1) of the above polymer was prepared in an identical manner from monomer of higher purity. In this case the polymer had $\eta_{sp/c}$ = 1.23 dl/g and Tg = 200°C.

7.2.4 TMBA Polyestercarbonate (AF-TP-1C)

A mixture of TMBA in aqueous base containing triethylamine was prepared as in the previous experiment. A solution of terephthaloyl chloride (10.15 g, 0.05 mole) in dichloromethane (140 ml) was then added in a single portion and the resultant two-phase system stirred at 300 rpm for 5 minutes. At this time phosgene gas was admitted to the vapor space so that after 70 minutes a pH of 7-8 was obtained for the aqueous phase. Concentrated aqueous sodium hydroxide (30 ml, 0.5 mole) was added and the mixture stirred for an additional two hours, during which time the viscosity increased. The organic phase was worked-up as desribed before to yield 35 g (95%) of copolymer which had $\eta_{sp/c}$ = 1.43 dl/g (C = 0.5). phenol/TCE), 1.24 dl/g (C = 0.5 CH_2Cl_2). The composition of the copolymer was determined from the 60 MHz NMR spectrum ($CDCl_3$) as well as by IR [comparison of the 1770 vs 1740 cm^1 absorbance bands of solution cast films using the pure polycarbonate and terephthalate polyester of TMBA as calibration standards]. By both techniques the composition was 2:1:1 TMBA:Terephthalate:carbonate in the copolymer which corresponds exactly to the monomer feed ratio. The Tg of the copolymer was 223°C (DSC) with no indication of melting below 375°C. Steady weight loss in TGA (argon) started at 300°C with major decomposition taking place above 400°C.

7.2.5 TMDCB Polycarbonate (AF-TP-2A)

A slurry of TMDCB monomer (20.13 g, 0.05mole) in a solution comprised of distilled deoxygenated water (250 ml), sodium hydroxide (16 g, 0.4 mole), sodium dithionite (0.1 g) and triethylamine (0.7 ml, 0.005 mole) was prepared under a nitrogen atmosphere. Dichloromethane (150 ml) was added and the mixture stirred at 300 rpm at 20-25°C while phosgene was admitted as described before. After the pH of the aqueous phase had reached 10, all solid monomer was dissolved and both phases were clear. Phosgene addition was continued until the pH approached 7. At this time aqueous sodium hydroxide (50 ml, 0.4 mole) was added and the polycondensation was allowed to proceed for three hours. The mixture was then diluted with water (150 ml) and dichloromethane (110 ml). The organic phase was separated and worked-up by the washing and precipitation methods discussed previously. The yield of dry polymer was 18 g with $\eta_{sp/c}$ = 1.93 dl/g (C = 0.5, CH_2Cl_2). The polymer was insoluble in phenol/TCE. Elem. anal.

calcd ($C_{29}H_{32}O_3$) %C = 81.27, %H = 7.53; found %C = 81.14, %H = 7.55. The 60 MHz NMR spectrum ($CDCl_3$) showed a singlet at 1.61δ (aliphatic gem - CH_3), a singlet 2.22δ (aromatic CH_3) a singlet at 6.88δ (aromatic protons ortho to CH_3) and a singlet at 7.06δ (center aromatic ring protons). The integration ratio was 12:12:4:4 as required by the proposed structure. The Tg of the polymer was 190°C (DSC) with no indication of melting below 350°C. The polymer was thermally stable up to 275°C with major decomposition occurring above 400°C.

7.2.6 TMDCB terephthalate (AF-TP-2B)

This polymer was prepared by the same interfacial method used for the corresponding TMBA terephthalate. The polymerization was conducted on 0.2 mole scale of TMDCB (40.26 g). The yield of polymer with $\eta_{sp/c}$ = 1.01 dl/g (C = 0.5, $CHCl_3$) was essentially quantitative. The polymer was only partially soluble (swollen) by phenol-TCE. Elem. anal. calcd $(C_{36}H_{36}O_4)_n$ %C = 81.17, %H = 6.81; found %C = 81.31, %H = 6.93. The Tg (DSC) of the material was 228°C. Steady weight loss in TGA (argon) began at 350°C.

7.2.7 TMDCB Polyestercarbonate (AF-TP-2 series)

7.2.7.1 Two Stage Interfacial Method (AF-TP-2, 2-1)

A slurry of TMDCB monomer in the aqueous solution was prepared as in the above experiment 7.2.5, except that the amount of sodium hydroxide used initially was 6 g (0.15 mole). Dichloromethane (100 ml) was added under the same conditions of stirring and temperature followed by a solution of terephthaloyl chloride (5.075 g, 0.025 mole) in dichloromethane (150 ml). After five minutes, phosgene gas was admitted under stirring until the pH reached 7 (30 minutes). Aqueous sodium hydroxide (20 ml, 0.15 mole) was added and phosgenation was continued until the pH again reached 7 (45 minutes). At this point additional aqueous sodium hydroxide (60 ml, 0.45 mole) was added and polycondensation allowed to proceed for three hours. During this time the viscosity of the mixture became so high that dilution with dichloromethane (100 ml) became necessary. The mixture was diluted with water (200 ml) and worked-up as described previously. The yield of dry copolymer was 23.3 g with $\eta_{sp/c}$ = 1.8 dl/g (C = 0.5 CH_2Cl_2). The ratio of TMDCB/terephthalate/-carbonate in the copolymer was 2:1:1 by the IR technique described previously. The Tg was 210°C (DSC) with no evidence of melting below 375°C. The TGA showed that major decomposition of the copolymer started at about 400°C.

A lower molecular weight and larger scale version of the above was prepared in the following manner.

A slurry of purified TMDCB monomer (92.6 g, 0.23 mole) in a solution containing distilled deoxygenated water (1150 ml), sodium hydroxide (27.6 g, 0.69 mole), sodium dithionite (0.46 g) and triethylamine (3.2 ml, 0.023 mole) was prepared in a 5 l flask under a nitrogen atmosphere. Distilled dichloromethane

(460 ml) was added and the mixture was stirred at 300 rpm at 25°C. A filtered solution of purified terephthaloyl chloride (23.3 g, 0.115 mole) in dichloromethane (460 ml) was then added rapidly to the flask. After ten minutes, a solution of p-t-butyl phenol (0.52 g, 1.5 mole % on TMDCB) in dichloromethane (230 ml) was added followed by phosgene gas. The phosgene was added until the pH of the aqueous phase reached 7 (60 min). Additional sodium hydroxide was then added as a 50% aqueous solution (24 g NaOH) and phosgenation continued until the pH dropped to 8. At this point, the final addition of sodium hydroxide was made (54 g) and the polycondensation was allowed to proceed for 3.5 hours at 25°C under continuous stirring. The polymer phase was worked up by successive water washing, although the presence of a stable water-polymer solution emulsion precluded an effective washing. The polymer phase was then acidified with aqueous acetic acid and washing was continued until the pH of the polymer phase was about 6. The polymer was isolated by precipitation in 2-propanol. The yield of dry polymer was 96 g with $\eta_{sp/c}$ = 0.67 dl/g (C = 0.5, CH_2Cl_2); Tg = 207°C, and TGA showing decomposition in a single step above 400°C. The ratio of TMDCB to terephthalate in the final polymer was 2:1 as measured by IR spectroscopy. The elemental analysis was also in agreement with the above IR analysis.

7.2.7.2 Combination Solution - Interfacial Method (AF-TP-2-2, 2-3)

A solution of pure TMDCB (20.13 g, 0.05 mole) was prepared in a mixture of distilled dichloromethane (100 ml) and anhydrous pyridine (12.07 ml, 0.15 mole) under a nitrogen atmosphere. To this solution pure terephthaloyl chloride (5.075 g, 0.025 mole) dissolved in distilled dichloromethane (75 ml) was added rapidly at 25°C with good stirring. After two hours at 25°C the homogeneous solution was washed twice with 200 ml of 5% aqueous HCl followed by water until neutral. The clear water-white solution was then placed in a reaction flask containing a solution of distilled deoxygenated water (250 ml), sodium hydroxide (8 g, 0.2 mole) and triethylamine (0.35 ml, 0.0025 mole). The mixture readily formed an emulsion upon stirring at 300 rpm. Phosgene gas was then added until the pH of the aqueous phase was 8 (45 min.). At this point aqueous sodium hydroxide (0.05 mole, 25 ml) was added to return the pH to >12 and the polycondensation stage was allowed to proceed with stirring for an additional 3 hours. [In experiments employing chain regulator, the addition of p-t-butyl phenol was made after the first 15 min. of phosgene addition]. At the end of polycondensation 3 mole % of p-t-butyl phenol (based on TMDCB) was added for end-capping. After at least 20 min. the stirrer was stopped, and immediate phase separation occurred. The polymer phase was then washed successively with water until the pH was ≤8 and the washings gave a negative response to chloride ion with aqueous silver nitrate. The polymer phase as acidified with dilute acetic acid, and washing was continued until the pH was 6-7. Polymer was isolated by precipitation into 2-propanol followed by vacuum drying at 120°C. The polymer was then redissolved in dichloromethane (5 to 10%

solution), and the resultant clear solution was washed several times with water. The final polymer was obtained by reprecipitation in 2-propanol. The yield of dry polymer was 21 g with η_{sp}/C = 4.06 dl/g (C = 0.5, CH_2Cl_2). The TG was 214°C. TGA showed decomposition in a single step above 400°C. The ratio of TMDCB to terephthalate in the final polymer was 2:1 as determined by IR spectroscopy. Several scale-up runs of this preparation were made (100 g batches) for which more practical molecular weights were obtained (1 dl/g). The following is an illustrative preparation (AF-TP-2-3).

A solution of pure TMDCB (104.8 g, 0.26 mole) was prepared in a mixture of distilled dichloromethane (520 ml) and anhydrous pyridine (41.9 ml, 0.52 mol) under a nitrogen atmosphere. To this solution recrystallized terephthaloyl chloride (26.39 g, 0.13 mole) dissolved in distilled dichloromethane (390 ml) was added rapidly with good stirring at 25°C (the TPC solution was filtered before addition). After four hours at 25°C, the substantially homogeneous solution was washed three times with 750 ml portions of 5% aqueous HCl followed by water until neutral.

The above oligomer solution was placed in a 5 l reaction flask equipped with mechanical stirrer, gas addition inlet and gas outlet connected to a series of traps containing aqueous potassium hydroxide. A solution containing distilled deoxygenated water (1300 ml), sodium hydroxide (41.6 g, 1.04 mol) and triethylamine (1.82 ml, 0.013 mol) was then added to the flask. The mixture was stirred at 300 rpm to form an emulson, and phosgene gas was admitted through the inlet tube at a flow rate of

"100" on a #601 Rotameter (MC&B). After 15 minutes of phosgene addition a soluton of p-t-butylphenol (0.292 g, 0.0019 mole, 0.75 mole % on TMDCB) in 5 ml of dichloromethane was added to the reaction mixture. Phosgene addition was continued until the pH of the aqueous phase dropped to 6 (75 min, total time). The pH of the aqueous phase was raised to about 11 with more sodium hydroxide (21 g, 0.51 mol in 50 ml water) and polycondensation was allowed to proceed for 4 hours at 25°C under rigorous agitation. Excess p-t-butylphenol (1.2 g) was added at the end of polycondensation. The viscous clear polymer phase which separated immediately upon stopping the stirrer was then washed successively with water until the pH was ≤ 8 and the washings gave a negative response to chloride ion with aqueous silver nitrate. The polymer phase was acidified with dilute acetic acid, and washing was continued until the pH was 6-7. Polymer was isolated by precipitation into 2-propanol followed by vacuum drying at 120°C. The polymer was the redissolved in dichloromethane (5 to 10% solution), and the resultant clear solution was washed several times with water. The final polymer was obtained by re-precipitation in 2-propanol. The yield of dry polymer was 110 g with $\eta_{sp}/C = 0.98$ dl/g. The Tg was 203°C. TGA showed decomposition in a single step above 400°C. The ratio of TMDCB to terephthalate in the final polymer was 2:1 as determined by IR spectroscopy. The elemental analysis was in agreement with the IR results: found %C = 81.01, %H = 7.27. The NMR spectrum also showed the relative proportions of TMDCB to terephthalate residues to be 2:1.

7.2.8 TMDCB Copolyestercarbonates (AF-TP-3 to 6-3)

7.2.8.1 AF-TP-4 (20% BPA)

This preparation is representative of AF-TP-3, 4, 5 and 6-1 in which all the bisphenol-A was added during the polyester oligomer forming step.

TMDCB (16.1 g, 0.04 mole) and bisphenol-A (2.3 g, 0.01 mole) were dissolved in a mixture of distilled dichloromethane (100 ml) and anhydrous pyridine (12.07 ml, 0.15 mole) under nitrogen. A solution of terephthaloyl chloride (5.075 g, 0.025 mole) in dichloromethane (75 ml) was then added rapidly at 25°C with stirring. The solution was allowed to stir for a period of 30-60 minutes until the initial deep yellow color had faded. The oligomer solution was then washed several times with dilute aqueous HCl to remove pyridine and the hydrochloride salt. After several water washings the aqueous phase gave a negative response for chloride ion to dilute silver nitrate solution.

The oligomer solutions (or in the case of AF-TP-6-1, a slurry) was stirred at 300 rpm with a solution comprised of deoxygenated distilled water (250 ml), sodium hydroxide (8 g, 0.2 mole) and triethylamine (0.35 ml, 0.0025 mole). After 15 minutes of phosgene addition, a solution of p-t-butyl phenol (0.057 g, 0.75 mole %) in dichloromethane (2 ml) was added. Phosgenation was continued for 45 minutes at which time the pH had reached 8-9. Aqueous sodium hydroxide (0.1 mole, 25 ml) was added, and the polycondensation was allowed to proceed for an additional two hours. At this point, p-t-butyl phenol (0.23 g, 3 mole %) in dichloromethane (3 ml) was added. After 20 minutes the reaction mixture was diluted with 200 ml dichloromethane and was worked up as described above. The yield of final polymer was 21 g with η_{sp}/C = 1.10 dl/g (C=0.5, CH_2Cl_2). The Tg was 208°C and the TGA showed major decomposition in a single step above 400°C. The ratio of total bisphenols to terephthalate was 2:1 by IR spectroscopy. The ratio of TMDCB to BPA was estimated by nmr spectroscopy (4:1).

This procedure operated well for copolymers containing up to 30 mole % BPA. However, in the case of copolymers with 40 mole % BPA or greater, the inhomogeneity of the oligomer preparations led to materials having a high content of infusible particles which gave rise to high haze values for molded specimens. As a result a modified procedure was developed in which a portion of the BPA was withheld from the oligomer and added before the polycondensation step. The following preparation is illustrative of the technique.

7.2.8.2 AF-TP-6 (40% BPA)

TMDCB (50 g, 0.124 mole) and bisphenol-A (12.1 g, 0.053 mole) were dissolved in a mixture of distilled dichloromethane

(354 ml) and anhydrous pyridine (49.9 ml, 0.62 mole) under nitrogen. A solution of terephthaloyl chloride (21 g, 0.1035 mole) in dichloromethane (295 ml) was then added rapidly at 25°C with stirring. The homogeneous solution was washed as in the previous preparation. The composition of the oligomer in terms of relative mole % bisphenols was at this point 70 mole % TMDCB, 30 mole % BPA.

The above oligomer solution was stirred at 300 rpm with a solution comprised of deoxygenated distilled water (1033 ml), sodium hydroxide (33.1 g, 0.83 mole), triethylamine (1.48 ml, 0.0103 mole) and bisphenol-A (6.85 g, 0.03 mole). After 15 minutes of phosgene addition, a solution of *p*-*t*-butylphenol (0.233 g, 0.75 mole %) in dichloromethane (5 ml) was added. Phosgenation was continued for 60 minutes at which time the pH had reached 6. Aqueous sodium hydroxide (16 g, 0.4 mole in 50 ml water) was added, and the polycondensation was allowed to proceed for an additional four hours. At this point, *p*-*t*-butylphenol (0.62 g, 2 mole %) in dichloromethane (10 ml) was added. After 20 minutes the reaction mixture was worked up as described above. The yield of final polymer was 78 g with $\eta_{sp}/C = 1.00$ dl/g. The Tg was 200°C and the TGA showed major decomposition in a single step above 400°C. The ratio of total bisphenols to terephthalate was 2.05:1 by IR spectroscopy. The mole fraction of TMDCB to total bisphenols was estimated by nmr spectroscopy (≈0.6). The elemental analysis was in good agreement with the above results: found %C = 80.05, %H = 6.62.

In a similar manner copolymers having 50 and 60 mole % BPA were prepared. In both cases the ratio of total bisphenols to terephthalate was close to 2:1 by IR measurements and the mole fraction of TMDCB to total bisphenols was 0.5 and 0.4, respectively, by nmr spectroscopy. The Tg values were 195 and 191°C, respectively.

7.2.9 TMDCB Copolyester (AF-TP-7)

TMDCB (20.13 g, 0.05 mole) was added to a solution of sodium hydroxide (6g, 0.15 mole), benzyltriethylammonium chloride (0.36 g) and sodium dithionite (0.07 g) in distilled deoxygenated water (178.5 ml) with stirring under a nitrogen atmosphere at 25°C. Dichloromethane (36 ml) was added followed by a solution of terephthaloyl chloride (5.07 g, 0.025 mole) and isophthaloyl chloride (5.075 g, 0.026 mole) in dichloromethane (142.5 ml) which was added dropwise over 30 minutes. During addition and throughout the preparation the two phase mixture was stirred at 300 rpm. After one hour p-t-butylphenol (0.3 g) was added and stirring wss continued for another one hour. The copolymer solution was washed several times with water to remove salts and was mildly acidified with a few drops of glacial acetic acid. The substantially clear copolymer solution was then precipitated in a 10-fold volume excess of 2-propanol in a blender. The precipitated copolymer was vacuum dried at 120°C. The yield was 25 g.

η_{sp}/C = 0.98 dl/g (C = 0.5); Tg = 212°C by DSC and TGA 400°C. The elemental analysis was consistent with the predicted structure: found %C = 81.41, %H = 6.71.

7.2.10 DCB Polycarbonate (AF-TP-8)

Purified dicumylbisphenol (69.28 g, 0.2 mole) was dissolved in a solution of anhydrous pyridine (49 ml, 0.6 mole) in dichloromethane (600 ml) at 25°C in a nitrogen atmosphere. Phosgene gas was then added at a rate of 0.25 g/minute with stirring (MC&B #601 Rotameter) until the viscosity of the solution began to increase markedly. At this point phosgene addition was terminated and p-t-butylphenol (0.1 g) was added to end-cap the polymer. The polymer solution was then precipitated into a 10 volume excess of methanol in a blender, followed by washing with water at 80°C. The polymer was vacuum dried at 110°C for 36 hours. The yield was 70 g. η_{sp}/C = 1.80 dl/g (C = 0.5, CH_2Cl_2). The Tg (DSC) was 156°C and TGA showed the onset of accelerated decomposition at 400°C. Elem. anal. found %C = 80.54, %H = 6.39. The nmr spectrum was consistent with the proposed structure and with the exception of line broadening was essentially identical to that of the DCB monomer.

7.2.11 DCB Terephthalate (AF-TP-8A)

Purified DCB (34.64 g, 0.1 mole) was dissolved in a solution of pyridine (24.5 ml, 0.3 mole) in dichloromethane (300 ml) under nitrogen at 25°C. A freshly prepared solution of terephthaloyl chloride (20.3 g, 0.1 mole) in dichloromethane (100 ml) was then added dropwise with good stirring over a period of 30 minutes. During the addition polymer precipitated as a coarse powder. The heterogeneous mixture was allowed to stir for an additional hour before precipitation into 2-propanol. The yield of dry polymer was 48 g. The material was substantially insoluble in the usual solvents at 25°C (CH_2Cl_2, phenol-TCE) and was shown to be quite crystalline by x-ray analysis.

This preparation was repeated with chloroform as the solvent. In this case much more of the polymer remained in solution. However, during vacuum drying of the precipitated polymer, crystallization occurred to such an extent that solubility and fusibility again was limited.

7.2.12 BPA-4,4'-BDA Polyester (AF-TP-9 Series)

7.2.12.1 Solution Method

A solution of pure bisphenol-A (3.196 g, 0.014 mole) was prepared in anhydrous pyridine (4.50 ml, 0.056 mole) and methanol free anhydrous chloroform in a flask fitted with a mechanical stirrer, nitrogen gas inlet, dropping funnel and water bath at 25°C. The solution was kept under a blanket of nitrogen gas throughout the reaction. A solution of 4,4'-benzophenone dicarboxylic acid chloride (4.30 g, 0.914 mole) was prepared in chloroform (80 ml) and was added dropwise at 25°C to the bisphenol solution over a period of 1/2 hr. with stirring. The reaction mixture was then precipitated in a ten volume excess of methanol in a blender. The polymer powder was collected by filtration, washed with water and dried in a vacuum oven. The polymer was further purified by dissolution in chloroform (10% solution) and reprecipitated from methanol. The yield was 6 g, η_{sp}/C = 0.42 dl/g (phenol/TCE), Tg = 180°C by DSC. Elem. anal. calcd. for $(C_{30}H_{22}O_5)_n$, %C = 77.91, %H = 4.79; found %C = 77.41, %H = 4.73.

7.2.12.2 Interfacial Method

The following reagents were dissolved in 500 ml of distilled deoxygenated water under nitrogen: pure bisphenol-A (32.0 g, 0.140 mole), sodium hydroxide (16.8 g, 0.42 mole), sodium dithionite (0.1 g) and benzyl triethyl ammonium chloride (0.1 g). This solution was added to a flask fitted with a mechanical stirrer, nitrogen gas inlet, dropping funnel and water bath at 25°C. With good agitation (300 rpm) anhydrous dichloromethane (150 ml) was added followed by a solution of 4,4'-benzophenone dicarboxylic acid chloride (43.0 g, 0.14 mole) in dichloromethane (600 ml). The acid chloride solution was added over a period of 1/2 hr. After stirring an additional 45 minutes the viscosity of the solution had increased markedly. Water (1 l) containing 50 ml of 2-propanol was added to the mixture and the clear polymer phase was separated and washed several times with water, 2% aqueous acetic acid and finally water until the pH of the aqueous phase was about 5-6. The polymer was isolated by precipitation into methanol as in the previous preparation. The material was reprecipitated once more and dried in a vacuum oven at 110°C. The yield was 60 g with η_{sp}/C = 1.13 dl/g (phenol/TCE). The Tg was 210°C. TGA analysis showed the onset of rapid decomposition at about 400°C. Elem. anal. calcd. for $(C_{30}H_{22}O_5)_n$, %C = 77.91, %H = 4.79, found %C = 77.63, %H = 4.79.

The polymers from both solution and interfacial polycondensations gave identical IR and nmr spectra which were consistent with the required polymer structure. The nmr spectra ($CDCl_3$) showed a singlet at 1.80 δ (broad, CH_3); and AA'BB' pseudoquartet centered at 7.25 δ (phenyls of BPA) and an AA'BB' pseudoquartet centered at 8.15 δ (phenyls of 4,4'-BDA) with an integration ratio of 6:8:8 as required.

7.2.13 DCB-4,4'-BDA Polyester (AF-TP-9A)

This polyester was prepared by the interfacial method described above for the BPA polyester. The resultant polymer was of very low molecular weight (η_{sp}/C = 0.13 dl/g), and the Tg value was also low (150°C). When the experiment was repeated with chloroform as the polymer phase solvent the η_{sp}/C was raised to 0.52 dl/g and the Tg to 190°C. The higher molecular weight material (AF-TP-9A-1) gave an elem. anal. of %C = 80.81, %H = 5.58. For this material the IR and nmr spectra were consistent with the structure. The nmr spectrum ($CDCl_3$) showed a singlet at 1.75 δ (CH_3), a multiplet centered at 7.25 δ (phenyls of DCB) and an AA'BB' pseudoquartet centered at 8.15 δ (phenyls of 4,4'-BDA) in a ratio of 12:12:8.

7.2.14 TMDCB-4,4'-BDA Polyester (AF-TP-9B)

This polyester was also prepared by the interfacial method employed for the DCB analog with chloroform as the polymer phase solvent. The final polymer had $\eta_{sp}/C = 0.50$ dl/g and a Tg of 206°C. TGA showed rapid decomposition above 400°C. Elem. anal. was consistent with the structure - %C = 81.28, %H = 6.49. IR and nmr spectra were also in agreement with the required structure. The nmr spectrum ($CDCl_3$) showed a singlet at 1.7 δ (isopropylidene CH_3), a singlet at 2.2 δ (phenyl CH_3), a multiplet centered at 7.1 δ (phenyls of TMDCB) and an AA'BB' pseudoquartet centered at 8.2 δ (phenyls of 4,4'-BDA) in a ratio of 12:12:8:8.

7.3 Preparation and Characterization of TMDCB-Terephthalate Oligomers

7.3.1 Interfacial Method

Reactions of TMDCB and terephthaloyl chloride were conducted on a 0.005 mole scale as in the first stage of AF-TP-2 preparation described in section 7.2.7.1. In all cases the ratio of TMDCB to TPC was 2:1. The oligomers were isolated after appropriate reaction times by removing the dichloromethane phase, washing with water until neutral and evaporating the solvent on a rotoevaporator. The reduced specific viscosities of these oligomers were then measured (results shown in Table 2).

7.3.2 Solution Method

In a typical preparation TMDCB monomer (2.013 g, 0.005 mole) was dissolved under a nitrogen atmosphere in distilled dichloromethane (10 ml) containing dry pyridine (0.12 ml, 0.015 mole). To this colorless homogeneous solution, terephthaloyl chloride (0.5075 g, 0.0025 mole) dissolved in dichloromethane (7.5 ml) was added rapidly at 25°C. The solution immediately became a deep yellow color which faded over a period of 30 to 60 min., as the reaction went to completion. After appropriate reaction times the homogeneous oligomer solutions were washed in a separatory funnel several times with dilute aqueous HCl to remove pyridine and the hydrochloride salt, and then with water until the washings showed no response of chloride ion to aqueous silver nitrate. The oligomers were isolated by evaporation of the solvent on a rotoevaporator. The solution viscosities were measured and the results compared with the interfacial method above (see Table 2).

7.4 Calibration Curve for Regulator and End Capping

AP-TP-2 preparations were conducted on 0.05 mole scale (TMDCB) with p-t-butyl phenol as the chain regulator. In most cases, the appropriate amount of regulator, based on TMDCB, was added during the first one-third of phosgene addition. In all experiments, the regulator was added as a solution in dichloromethane. At the end of the polycondensation stage, end-capping was accomplished by the addition of 3 mole % more of p-t-butyl phenol in dichloromethane. Reaction mixtures were then allowed to stir for at least 20 min. before work-up. Solution viscosity results were employed in the constructon of the calibration curve shown in Figure 2. In the case of the curve depicted in Figure 3 which is for the combination solution-interfacial method, a similar technique was employed using small scale versions of AF-TP-2-2. The amount of regulator was varied as in the above case.

7.5 Polymer Characterization and Evaluation

7.5.1 Solution Viscosity Measurements

Dilute solution viscosities were measured at 25°C at polymer concentrations of 0.5 g/dl in Ubbelhode sizes 1C or 0C viscometers. In most cases the solvent was a 60/40 mixture of phenol and tetrachloroethane (size 1C). However, in some cases dichloromethane or chloroform were employed when the polymer solubility in phenol-TCE was limited (size 0C). In all cases the results are reported in terms of η_{sp}/C in units of dl/g.

7.5.2 Tg and TGA Measurements

Tg measurements were conducted on a DuPont 990 differential scanning calorimeter at a heating rate of 20°C/min in argon. In all cases the reheat technique was employed to check for changes in the transition temperature. TGA measurements were conducted on a DuPont 951 or Perkin Elmer TGS-2 thermogravimetric analyzer at a heating rate of 10°C/min in argon. In all cases the reported temperatures were taken as the maximum rate of accelerated decomposition from the differential of the weight loss vs temperature curves.

7.5.3 IR Spectra

Infrared spectra were obtained from either solvent cast films or KBr pellets on a Perkin-Elmer 283 Spectrometer. The cast films were prepared by the draw down technique from 20% solutions in dichloromethane or chloroform. Pellets were prepared from solution precipitated powders. For the determination of the ester to carbonate ratio in polyestercarbonates calibration curves were constructed from the pure polyester and polycarbonate homopolymers by comparison of the absorbance bands at 1770 and 1740 cm^{-1} which are characteristic of aromatic carbonate and aromatic ester carbonyl stretching modes. For the calibrations the absorbance ratios of 1770/1740 cm^{-1} bands were plotted against the mole ratios of carbonate/ester in the polymer blends. The unknowns of each particular polymer type were then calculated from the observed absorbance ratio and the corresponding calibration curve. From the determined CO_3/CO_2 value the ratio of aromatic diol to diacid in the polymer could be easily calculated.

7.5.4 NMR Spectra

All spectra were recorded on a Varian T-60 (60 MHz) spectrometer in the proton mode. In most cases deuterochloroform ($CDCl_3$) was used as the solvent. All chemical shift values are relative to tetramethysilane (TMS) as the internal standard.

7.5.5 Optical Measurements

Transmittance, haze and color (yellowness index) values were determined in accordance with ASTM-D1925 using a Hunterlab Color/Difference Meter #D25D2 with D25D optical head at 70°F and 50% relative humidity (RH). Test specimens were of 1/8" thickness and were fabricated by compression molding using an Industrial Hydraulic Machine Co. press. Typical molding conditions employed were 320°C for 6 minutes between Appollo plates (chrome plated steel) with slow creep to 0.5 tons pressure and cooling in the press at 7 tons pressure. In cases where the melt viscosities of materials were low at 320°C, the temperature was lowered to 280-300°C.

All numerical values obtained are with respect to the following definitions. Transmittance (luminous transmittance) is the ratio of transmitted to incident light, expressed in percent. Haze is the percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering. The yellowness index (YI) is the magnitude of yellowness relative to magnesium oxide for CIE Source C. In this test method yellowness is defined as the deviation in chroma from water-whiteness in the wavelength range from 570 to 580 nm. The YI obtained by this method corresponds well with the magnitude of yellowness perceived under daylight illumination.

7.5.6 Tensile Measurements

All tensile measurements were obtained using ASTM Type V specimens at a thickness of 1/32" in order to conserve polymer samples. In most cases the evaluation included measurement of yield elongation (YE), yield strength (YS), ultimate elongation (UE), ultimate tensile strength (UTS) and tensile modulus (M), all expressed in % or psi. Test method ASTM-D638 was employed with a constant rate of extension instrument (Instron) at a head speed of 0.05 inches/min in a controlled environment (70°F, 50% RH). Test specimens were cut from compression molded sheets obtained on an Industrial Hydraulic Machine Co. press. Typical molding conditions were 320°C for 5 minutes with creep to 5 tons pressure followed by cooling in the press at 20 tons pressure. In some cases where lower molding temperatures (310°C) had to be used the creep pressure was increased to 15 tons. The reference materials (Lexan®, Polysulfone) were fabricated and tested under identical conditions. The results are averages of at least seven runs for all materials.

7.5.7 IZOD Impact Measurements

All IZOD impact measurements were obtained on 1/8" thick specimens having standard notch geometry under conditions specified in ASTM-D256 (Method A). A Baldwin Impact Tester was employed at 70°F and 50% RH. In certain cases where unnotched impact strength was evaluated, the sample was struck on the reverse side. For most materials the average of seven or more runs is reported. Specimens were machined from compression molded plaques obtained on an Industrial Hydraulic Machine Co. press under the following conditions: 320°C for 10 minutes with creep to 2 tons pressure followed by cooling in the press at 7 tons pressure. For most polymer materials covered in this report the mode of failure during the IZOD test was mode C (complete break). The reference materials were fabricated and tested in the same manner.

7.5.8 Heat Deflection Temperature Measurements

Heat deflection temperatures (HDT) were determined on 1/4" thick test bars according to ASTM-D648. A Custom Scientific Co. apparatus was employed at 264 psi (1820 kPa) fiber stress with a heating rate of 2°C/min. In all cases the reported values are for a deflection of 0.01 inches (0.25 mm). All polymers were compression molded at 320°C for 15 min with creep to 2 tons pressure and cooling in the press at 10 tons pressure. The samples were conditioned after fabrication to 70°F and 50% RH.

7.5.9 Hydrolysis Resistance Studies

Selected AF-TP samples were compression molded into sheets at 320°C for 10 min with creep to 5 tons pressure and cooling in the press at 20 tons. For the reference materials, polyestercarbonate and Lexan®, the conditions were 310°C, 10 min to 5 tons, cooled at 20 tons and 300°C, 10 min to 5 tons, cooled at 20 tons, respectively. In all cases sheet thickness was kept reasonably constant at 0.4 mm (±0.05 mm). Prior to immersion in the hydrolyzing agents rectangular specimens 2 x 3 cm were cut from the sheets and accurately weighed. These specimens were then conditioned at 70°F and 50% RH for five days. For acid hydrolysis experiments the specimens were immersed in 5N aqueous hydrochloric acid at reflux (108°C), whereas for base hydolysis they were immersed in 5N aqueous sodium hydroxide at 80°C. At various time intervals the specimens were removed, thoroughly rinsed with distilled water and dried at room temperature. The specimens were then reconditioned at 70°F and 50% RH for ten days before being accurately reweighed. Weight loss per unit area values were determined. Reduced specific viscosity (η_{sp}/C values) was also determined on all surviving specimens at the end of 60 hours of exposure which was the limit of both tests.

8.0 REFERENCES

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