Polymers Containing the 9-Oxabicyclo[3.3.1]nonane Ring System

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ABSTRACT: Condensation polymers containing the 9-oxabicyclo[3.3.1]nonane ring system have been prepared from diamines, bisphenols, diisocyanates, and dicarboxylic acid derivatives with 2,6-dihydroxy-9-oxabicyclo-[3.3.1]nonane and its derivatives. Interfacial, solution, and modified melt polymerizations were utilized to prepare high molecular weight, film-forming polycarbonates, polyurethanes, polyesters, and polyester carbonates. In general, the polymers had water absorption and density values comparable with those of similar polymers derived from aromatic diols, with glass transition temperatures and melting points somewhat higher. Most of the products do not crystallize readily.

The application of the principle of cyclopolymerization has resulted in the preparation and characterization of a large number of addition polymers containing in-chain bicyclo ring systems.[1] For condensation polymerization, a much smaller number of such polymers has been reported[2] and meaningful comparisons of the effects of such ring systems on polymer properties have not been possible.

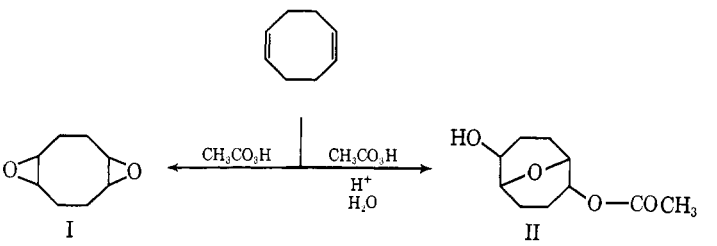
With preparation of 2,6-dihydroxy-9-oxabicyclo-[3.3.1]nonane, an intermediate was in hand which would permit the preparation of condensation polymers containing an in-chain bicyclo ring. This paper deals with the preparation and characterization of condensation polymers such as polycarbonates, polyesters, and polyurethanes containing the 9-oxabicyclo[3.3.1]nonane ring system.

Preparation and Characterization of 2,6-Dihydroxy-9-oxabicyclo[3.3.1]nonane. The addition of peroxyacetic acid in organic solvents, free of water and mineral acids, to *cis,cis*-1,5-cyclooctadiene has been reported[3] to yield the diepoxide, 1,2,5,6-diepoxycyclooctane (I). We have now found that, with commercial peroxyacetic acid, which is 40% peroxyacetic acid in acetic acid, containing approximately 1.0% sulfuric acid and 13% water, 2-acetoxy-6-hydroxy-9-oxabicyclo[3.3.1]nonane (II) was obtained in better than 85% yield (Scheme I).

The product (II), on hydrolysis, yielded 2,6-dihydroxy-9-oxabicyclo[3.3.1]nonane (III) in better than 90% yield. This diol was converted by conventional procedures into the corresponding diacetate (IV), bischloroformate (V), and the diphenyl (VI), diethyl (VII), and dimethyl (VIII) carbonates (Scheme II).

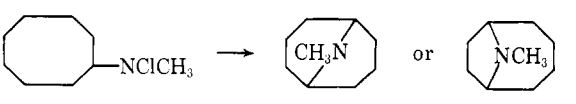
The structures of the compounds shown in Scheme I are supported by elemental analyses, molecular weight determinations, and hydroxyl numbers, where pertinent. The 9-oxabicyclo[3.3.1]nonane structure, as opposed to the isomeric 9-oxabicyclo[4.2.1]nonane structure, is strongly suggested by steric considerations and by a comparison of the infrared spectra with those of tetrahydrofuran and tetrahydropyran.

SCHEME I



I II

The steric assignment is further supported by the cyclization of N-chloro-N-methylcyclooctylamide to a similar bicyclo structure.[4] Although cyclization of this amine to IX involves closure to a bridged piperidine structure, this is the only product isolated and, in yields as high as 23%, after only 30 min reaction period.



IX X

(1) (a) G. B. Butler and R. I. Angelo, *J. Amer. Chem. Soc.*, **79**, 3128 (1957); (b) C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957); (c) C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, **25**, 1641 (1960); (d) G. B. Butler and R. W. Stachman, *ibid.*, **25**, 1643 (1960); (e) G. B. Butler, *J. Polym. Sci.*, **48**, 279 (1960); (f) D. T. Trifan and J. J. Hoglen, *J. Amer. Chem. Soc.*, **83**, 202 (1961); (g) A. H. Frazer and W. P. O'Neill, *ibid.*, **85**, 2613 (1963).

(2) (a) J. C. Caldwell and E. H. Hill, U.S. Patent 2,732,369 (Jan 24, 1956); 2,899,412 (Aug 11, 1959); (b) W. J. Jackson, Jr., and J. R. Caldwell, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 246 (1963); (c) E. P. Goldberg, *J. Polym. Sci., Part C*, **4**, 707 (1963); (d) K. P. Perry, W. J. Jackson, Jr., and J. R. Caldwell, *J. Appl. Polym. Sci.*, **9**, 3451 (1965); (e) R. C. Slagel, G. P. Shulman, and F. M. Young, *Ind. Eng. Chem., Prod. Res. Develop.*, **6**, 100 (1967); (f) P. W. Morgan, *J. Polym. Sci., Part A-1*, **2**, 437 (1964).

(3) F. C. Frostick, Jr., and B. Phillip, British Patent 793,150 (April 1958), *Chem. Abstr.*, **52**, 18268 (1958).

(4) S. Wawzonek and P. J. Thelane, *J. Amer. Chem. Soc.*, **72**, 2118 (1950).

The infrared spectra of all of these compounds are quite similar to that of tetrahydropyran with principal absorptions in the 9.26–9.8-μ region[5] while the spectrum of tetrahydrofuran shows principal absorptions in the 9.1–9.3-μ regions.[6]

The difference in products obtained from peroxyacetic acid additions to *cis,cis*-1,5-cyclooctadiene would appear to indicate that different pathways were involved in these radical additions. However, the difference could arise from the subsequent reactions of a common intermediate.

The argument for a common intermediate is supported by the formation of 2-acetoxy-6-hydroxy-9-oxabicyclo[3.3.1]nonane (II) from the diepoxide (I). On treatment of I with acetic acid containing 1% sulfuric acid and 13% water, II was obtained in over 60% yields.

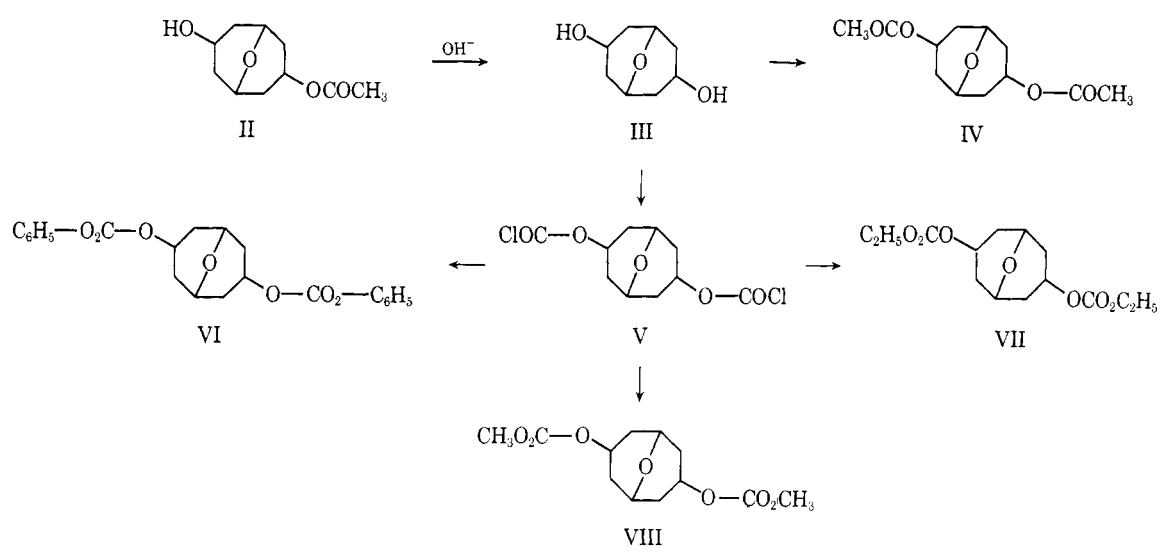
The reaction pathway might be considered as in Scheme III. This suggested pathway is analogous to that proposed for the cyclopolymerization of diepoxides.[7]

Polymers Containing the 9-Oxabicyclo[3.3.1]nonane Ring System. A. Polymerization. 1. Polycarbonates were prepared by interfacial,[8] modified interfacial,[9] and modified melt or solid phase polymerization. The highest molecular weights were obtained using the bischloroformate of II, V, in interfacial polymerizations utilizing 1,2-dichloroethane as the organic phase and sodium carbonate as acid acceptor or in modified interfacial polymerizations utilizing tetrahydrofuran as the organic phase with sodium carbonate as acid acceptor and tetraethylammonium chloride as the accelerator. A somewhat lower molecular weight polymer was obtained in solid phase polymerizations at 220° using diphenyl carbonate with triphenylphosphene as catalyst.

2. Polyurethanes were prepared by interfacial[8] and solution polymerizations.[9] The high molecular weight polymer was obtained by interfacial polymerization using V, 1,2-dichloroethane, as organic phase, and sodium carbonate as acid acceptor. A somewhat lower molecular weight polymer was obtained by solution polymerization using III and a diisocyanate in dimethyl sulfoxide or dimethylacetamide solutions with or without dibutyltin dilaurate as catalyst.

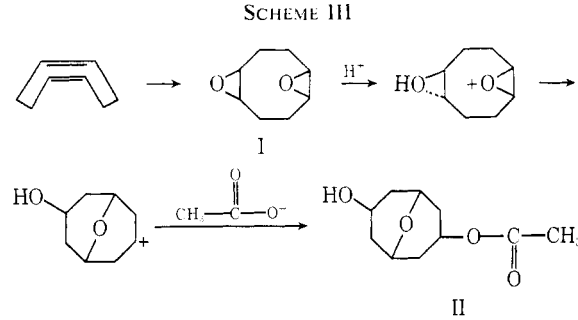
3. Polyesters and polyester carbonates were prepared by modified melt or solid phase polymerization. The polyesters were prepared from III or VII with triphenylphosphene or tetraisopropyl titanate as catalysts

SCHEME II



were prepared by interfacial,[8] modified interfacial,[9] and modified melt or solid phase polymerization. The highest molecular weights were obtained using the bis-

SCHEME III



at 220°. The polyester carbonates were prepared from the diphenyl carbonate of II, VI, under the same conditions. All attempts to prepare these polymers by melt polymerization were unsuccessful because of severe degradation at temperatures in excess of 235°.

B. Properties. 1. Polycarbonates. All the polycarbonates prepared were amorphous, as prepared, and

(5) S. C. Brecket and R. M. Badger, *J. Amer. Chem. Soc.*, **72**, 4397 (1958).

(6) G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

(7) (a) J. K. Stille and B. M. Culbertson, *J. Polym. Sci., Part A-1*, **2**, 405 (1964). (b) One of the referees has pointed out that the possibilities of *cis,exo*, *cis,endo*, *trans*, or a mixture of these isomers should be mentioned. The sharp melting points of III, IV, V, VI, and VII argue strongly that the alcohol is probably a single isomer. Preliminary attempts to determine the structure of this isomer by nmr spectroscopy have been inconclusive.

(8) E. L. Wittbecker and P. W. Morgan, *J. Polym. Sci.*, **40**, 289 (1959); P. W. Morgan and S. L. Kwolek, *ibid.*, **40**, 299 (1959); R. G. Beaman, P. W. Morgan, C. R. Koller, E. L. Wittbecker, and E. E. Magat, *ibid.*, **40**, 3231 (1959); V. E. Shashoua and W. M. Eaucham, *ibid.*, **40**, 343 (1959); E. L. Wittbecker and M. Katz, *ibid.*, **40**, 367 (1959); S. A. Sundet, W. A. Murphey, and S. B. Speck, *ibid.*, **40**, 389 (1959); W. M. Eareckson, *ibid.*, **40**, 399 (1959).

(9) P. W. Morgan and S. L. Kwolek, *ibid.*, *Part A-1*, **2**, 181 (1964); 209 (1964); 2693 (1964); 5149 (1964).

TABLE I

Polymers	Reactants[a] Derivative of II	Diol	Method[b]	η_{inh}[c]	PMT, °C[d]	Density (film)	Water absorption, % (film)
	A. Polycarbonates Containing the 9-Oxabicyclo[3.1.1]nonane Ring System						
IX	V	2,2-Bis(4-hydroxyphenyl)propane	A	1.05	280	1.245	0.32
X	V	Bis(4-hydroxyphenyl) sulfone	B	0.97	290	1.368	3.5
XI	VI	Resorcinol	C	0.50	270	1.273	2.3
XII	VI	Hydroquinone	C	0.53	310	1.251	1.1
XIII	VI	III	C	0.60	250	1.310	1.3
	B. Polyurethanes Containing the 9-Oxabicyclo[3.3.1]nonane Ring System	Other reactant					
XIV	V	Bis(4-aminocyclohexyl)methane (53% *trans,trans* isomer)	A	1.50	302	1.215	5.4
XV	V	Bis(4-aminocyclohexyl)methane (70% *trans,trans* isomer)	A	1.66	390	1.303	2.2
XVI	V	Piperazine	A	2.25	385	1.206	13.1
XVII	III	Bis(4-isocyanatophenyl)methane	D	0.70	285	1.330	2.2
	C. Polyester and Polyester Carbonates Contining the 9-Oxabicyclo[3.1.1]nonane Ring System	Other reactant					
XVIII	VI	Bis(hydroxyethyl) terephthalate	C	0.63	180	1.180	3.4
XIX	VI	Bis(hydroxyethyl)diurene dicarboxylate	C	0.53	295	1.210	2.3
XX	III	Diphenyl terephthalate	C	0.35	290	...	...
XXI	III	Dimethyl isophthalate	C	0.30	190	...	...

[a] See Scheme II for coding. [b] A, interfacial polymerization; B, modified interfacial polymerization; C, modified melt polymerization; D, solution polymerization. [c] Inherent viscosity of XV, XVI, and XVII determined in *m*-cresol, of XVIII in dimethyl sulfoxide, and of the remainder in *sym*-tetrachloroethane–phenol (40/60 by weight) at 0.5 g/100 ml and at 30°. [d] PMT (polymer melt temperature) was taken as the lowest point at which the polymer melted or left a trail under light pressure on a chrome-plated temperature gradient bar.

were readily soluble in chlorinated and aromatic hydrocarbons. All could be induced to crystallize by treatment with a near solvent, *i.e.*, acetone, but not by thermal treatments.

The polymer melt temperature (See Table I, footnote *d*) was found to vary with the molecular weight. In the case of the polymer derived from 2,2-bis(4-hydroxyphenyl)propane, IX, it ranged from 225° for η_{inh} of 0.32 to 250° for η_{inh} of 0.6 to a high of 290° for η_{inh} of 2.0.

Thin films of the polycarbonates had water absorptions ranging from 0.32 to 3.5% with densities from 1.220 to 1.368. The high water absorption value of 3.5% found for X, derived from bis(4-hydroxyphenyl) sulfone, probably reflects the presence of the polar sulfone group. The densities are in the range usually found for the all-aromatic polycarbonates.[10]

Films of the polycarbonates after exposure for 150 hr to ultraviolet light (Weather-Ometer) or to air at elevated temperatures (100–125°) showed no embrittlement, discoloration, or change in inherent viscosity. This stability was surprising in view of the presence of aliphatic ether linkages in these polymers. In past work, such linkages were found to be susceptible to thermal- and light-catalyzed oxidative attack with subsequent polymer degradation. The mechanism for this reaction is believed to involve hydroperoxide formation on the α-carbon followed by decomposition of the hydroperoxide with chain scission or with formation of unstable products.[11] In the case of polycarbonates, derived from III, hydroperoxide formation is certainly possible but subsequent decomposition pathways could not cause chain scission nor lead to products which could decompose with chain scission.

2. Polyurethanes. All the polyurethanes as prepared showed some crystallinity and were soluble only in such solvents as formic acid, chlorinated hydrocarbon mixtures, phenols, phenols–chlorinated hydrocarbons, dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. No significant variations in polymer temperature with molecular weight was observed for these more crystalline polymers.

Thin films of the polyurethanes had water absorption of 2.2–13.1 and densities of 1.206–1.303. The higher water absorption for these polymers over the polycarbonates reflects the greater polarity of the urethane linkage *vs.* the carbonate linkage. The densities are in the range usually found for polyurethanes derived from aromatic diols.[8,9]

Films of these polymers also exhibited excellent stability to ultraviolet light or air at elevated temperatures.

Polyester and Polyester Carbonates. The polyester derived from terephthalic and the polyester carbonates from terephthalic and durene dicarboxylic acids were crystalline whereas the polyester containing isophthalic acid was amorphous. The amorphous polymer was soluble in chlorinated and aromatic hydrocarbons; the

(10) W. F. Christopher and D. W. Fox, "Polycarbonates," Reinhold Publishing Corp., New York, N. Y., 1962; H. Schnell, "Chemistry and Physics of Polycarbonates," John Wiley and Sons, Inc., New York N. Y., 1964.

(11) O. B. Edgar and R. V. Hill, *J. Polym. Sci.*, **8**, 1 (1952); W. H. Charch and J. C. Shivers, *Textile Res. J.*, **29**, 536 (1959).

TABLE II
THERMAL BEHAVIOR OF POLYMERS

Polymer[a]	T_G, °C[b]	PMT, °C	Decompn temp, °C
IX	194	280	353
X	184	290	348
XIII	207	260	347
XIV	221	310	320
XV	229	396	390
XVI	113	388	350
XVII	200	295	287
XX	207	290	357
XXI	113	190	350

[a] See Table I for polymer coding. [b] Determined by a modified method of differential thermal analysis.[21]

crystalline polymers were soluble only in the strong polymer solvents listed in the previous section. Water absorptions and densities of thin films of polyester carbonates were in the range found for polyesters and polyester carbonates derived from aromatic diols.[8,10-12]

As in the case of the other polymers derived from III, films of these polymers showed no loss in inherent viscosity on exposure for 150 hr to ultraviolet light (Weather-Ometer) or to air at 100–125°.

Thermal Behavior. Since most of the polymers studied were amorphous, melting temperatures in some cases were rather broad. The polymer melt temperature (PMT), *i.e.*, the temperature at which the polymers would stick on the temperature gradient (T_G) bar under moderate pressure, was reasonably sharp and reproducible.

The polymers as a whole were high melting. All of the polycarbonates, polyesters, and those polyurethanes capable of hydrogen bonding had high T_G values (Table II). The polycarbonates had decomposition temperatures well above the polymer melt temperature whereas the polyurethanes decomposed below or near the PMT. Thus, films could be melt pressed from the polycarbonates but not the polyurethanes.

Film Properties. The melt processibility and the high T_G values of the polycarbonates suggested that they might be of interest in film applications. In Table III are summarized the properties of the polycarbonates, IX and X, along with properties of the polycarbonate from 2,2-bis(4-hydroxyphenyl)propane (XXII).

It is apparent that these films are practically equivalent in mechanical properties, with X somewhat inferior in electrical properties, probably due to the presence of the more polar sulfone group in the polymer chain. The higher T_G value (194°) for IX over XXII (150°) suggests a higher use temperature for films derived from this polymer.

Experimental Section

Preparation of 2-Acetoxy-6-hydroxy-9-oxabicyclo[3.3.1]nonane (II). A. From *cis,cis*-1,5-Cyclooctadiene. To 2300 g (11.04 mol) of commercial 40% peroxyacetic acid (FMC Corp., Inorganic Chemical Division) was slowly added 549 g (5.08 mol) of *cis,cis*-1,5-cyclooctadiene. During the addition and for 3 hr thereafter, the reaction mixture was maintained at −5–0°. After standing overnight, the excess acetic acid was removed under reduced pressure at a pot temperature of less than 40°. The residue, 2198 g, was neutralized with 785 ml of 20% sodium hydroxide solution. The neutralized solution was chilled to 0°, and the supernatant liquid decanted from the semisolid on the bottom of the reaction flask. The residual solid was dissolved in ethyl acetate, and the remaining water was azeotroped off. The ethyl acetate solution was filtered, and the ethyl acetate removed under reduced pressure. Distillation of the resdue gave 954 g of product (95.4% yield), bp 130–135° (0.8 mm), which, based on hydroxyl determination (one OH/molecule), had a molecular weight of 201 (theory, 200).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00; O, 32.00. Found: C, 60.05, 60.07; H, 7.98; 7.97; O, 32.10, 32.08.

The infrared spectrum (see Table IV) was consistent with that for the proposed structure.

B. From 1,2,5,6-Diepoxycyclooctane (I). A solution of 28 g of I[13] in 200 g of acetic acid containing 2 g of concentrated sulfuric acid and 26 g of water was stirred overnight at 40°. The excess acetic acid was neutralized with 53 ml of 20% sodium hydroxide solution. The neutralized solution was chilled to 0°, and the supernatant liquid decanted from the semisolid on the bottom of the reaction flask. The residual solid was dissolved in ethyl acetate, and the remaining water azeotroped off. The ethyl acetate solution was filtered, and the ethyl acetate removed under reduced pressure. Distillation of the residue gave 24 g of product (60% yield), bp 130–135° (8 mm), which, based on hydroxyl determination (one OH/molecule), had a molecular weight of 202 (theory, 200).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00; O, 32.00. Found: C, 60.20, 60.25; H, 7.96; 7.97; O, 31.85, 31.87.

The infrared spectrum (see Table IV) was consistent with that for the proposed structure.

Preparation of 2,6-Dihydroxy-9-oxabicyclo[3.3.1]nonane (III). A solution of 954 g of II in 1800 ml of 20% sodium hydroxide solution was refluxed overnight under nitrogen. The water was removed under reduced pressure, and the residue dissolved in 5 l. of boiling ethyl acetate and filtered. The filtrate was chilled in wet ice, and the crystals which were obtained were filtered off. After drying, 700 g (theory, 92% yield) of a white crystalline solid (mp 115–118°) was obtained. After two recrystallizations from ethyl acetate, a product, mp 128–129°, which had a molecular weight of 158, based on hydroxyl determination (theory, 158), was obtained.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.72; H, 8.94; O, 30.34. Found: C, 60.80, 60.82; H, 8.88, 8.89; O, 30.50, 30.51.

The infrared spectrum (see Table IV) was consistent with that for the proposed structure.

Preparation of 2,6-Diacetoxy-9-oxabicyclo[3.3.1]nonane (IV). A solution of 50 g of acetic anhydride and 31 g of III was refluxed overnight under nitrogen. The excess acetic anhydride and acetic acid were removed under reduced pressure and the residue was recrystallized from 2 l. of hot water. After drying, 40 g of a white crystalline solid, mp 99–100°, was obtained.

Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.46; H, 7.51; O, 33.03; mol wt (boiling point evaluation in benzene), 242. Found: C, 59.52, 59.56; H, 7.51, 7.53; O, 33.00, 33.02; mol wt, 241, 240.

The infrared spectrum (see Table IV) was consistent with that of the proposed structure.

Preparation of 2,6-Bis(chloroformyl)-9-oxabicyclo[3.3.1]nonane (V). To a solution of 350 g (3.5 mol) of phosgene in 2.5 l. of tetrahydrofuran was slowly added a solution of 100 g (0.63 mol) of III, 132 g (1.1 mol) of dimethylaniline, and 500 ml of tetrahydrofuran. During the addition and for 3 hr thereafter, the reaction mixture was maintained at 0–5° From the beginning of the addition, there was the immediate precipitation of a white solid which continued for the next 3

(12) H. Schnell, *Angew. Chem.*, **68**, 633 (1956); *Ind. Eng. Chem.*, **51**, 157 (1959); *Trans. Plastic Inst.*, **28**, No. 75, 43 (1960); H. Connix, *Ind. Eng. Chem.*, **51**, 147 (1959); P. W. Morgan, *J. Polym. Sci., Part A-1*, **2**, 437 (1964).

TABLE III
FILM PROPERTIES OF POLYCARBONATES

Property	ASTM test	Polycarbonates XXII[a]	IX[b]	X[c]
Thickness, mil		1.0	1.5	2.0
Tensile strength (psi × 10^3), MD	D-882	13.6	10.8	9.8
TD		11.4		
Modulus (psi × 10^3), MD	D-882	287	280	290
TD		250		
Elemendorf tear, (g), MD	D-689	7.7	6.5	6.0
TD		8.5		
Electrical insulation resistance (ohm cm)	D-257	9.17×10^{17}	8.3×10^{17}	1.45×10^{17}
Dielectric constant (10^{+3} cycles)	D-150	3.07	3.14	5.32
Dissipation	D-150	1.68×10^{-3}	1.80×10^{-3}	5.03×10^{-3}

[a] XXII, polycarbonate from 2,2-bis(4-hydroxyphenyl)propane. [b] IX, polycarbonate from 2,2-bis(4-hydroxyphenyl)propane and III. [c] X, polycarbonate from bis(4-hydroxyphenyl) sulfone and III.

TABLE IV
INFRARED ADSORPTION BANDS BETWEEN 9 AND 10 μ FOR COMPOUNDS PREPARED IN THIS STUDY

Compound	Wavelength, μ
II	9.26, 9.42, 9.63
III	9.30, 9.42, 9.48, 9.61
IV	9.15, 9.30, 9.45, 9.70
V	9.28, 9.48
VI	9.28, 9.48, 9.80
VII	9.30, 9.45
VIII	9.30, 9.40, 9.48, 9.57

hr. After standing overnight, the reaction mixture was filtered and the solvent and excess phosgene were removed under reduced pressure. The residue was recrystallized from 2 l. of petroleum ether (bp 35–70)°. After drying, 140 g (79% yield) of an off-white crystalline material was obtained. After two recrystallizations from petroleum ether, the product was a white crystalline solid, mp 101–102°.

Anal. Calcd for $C_{10}H_{12}O_3Cl_2$: C, 42.42; H, 4.28; O, 28.25; Cl, 25.05. Found: C, 42.98, 42.02; H, 4.10, 4.15; O, 28.70, 28.75; Cl, 25.18, 25.28.

The infrared spectrum (Table IV) was consistent with that for the proposed structure.

Preparation of 2,6-Bis(carboxyphenoxy)-9-oxabicyclo-[3.3.1]nonane (VI). To a Waring Blendor containing a solution of 300 ml of distilled water, 2.2 g (0.55 mol) of sodium hydroxide, 5.2 g (0.55 mol) of phenol, and 1.2 g of tetraethylammonium chloride was added, with vigorous agitation, a solution of 7.06 g (0.24 mol) of V in 150 ml of methylene chloride. The reaction mixture was rapidly stirred for 5 min and poured into 2 l. of water. The methylene chloride was removed with a nitrogen stream, and the residue recrystallized from ethyl alcohol. After drying, 8.7 g of crude diphenyl carbonate was obtained. After two recrystallizations from ethyl alcohol, a white crystalline solid, mp 130–131°, was isolated.

Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.31; H, 5.58; O, 28.11. Found: C, 66.20, 66.25; H, 5.75, 5.79; O, 28.55, 28.58.

The infrared spectrum (Table IV) was consistent with that for the proposed structure.

Preparation of 2,6-Bis(carboxymethoxy)-9-oxabicyclo-[3.3.1]nonane (VII). To a solution of 29.3 g (0.1 mol) of V and 300 ml of benzene was slowly added 400 ml of methanol. The resulting solution was refluxed overnight, and the benzene and excess methyl alcohol were removed under reduced pressure. After distillation, the residue was recrystallized from methanol and, after drying, 18 g (66% yield) of white solid was obtained. After two more recrystallizations from methanol, the product was a white crystalline solid, mp 81–82°.

Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.54; H, 6.63; O, 40.83. Found: C, 52.80, 52.81; H, 6.32; 6.41; O, 41.20, 41.26.

The infrared spectrum (Table IV) was consistent with that for the proposed structure.

Preparation of 2,6-Bis(carboxyethoxy)-9-oxabicyclo-[3.3.1]nonane (VIII). To a solution of 29.3 g (0.1 mol) of V and 300 ml of benzene was slowly added 400 ml of ethanol. The resulting solution was refluxed overnight and the benzene and excess methyl alcohol were removed under reduced pressure. On distillation, a 25-g (83% yield) fraction, bp 144–146° (0.8 mm), was obtained.

Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.61; H, 7.35; O, 37.04. Found: C, 55.85, 55.95; H, 7.15, 7.21; O, 37.20, 37.22.

The infrared spectrum (Table IV) is consistent with that for the proposed structure.

Preparation of Polycarbonate (IX). To a Waring Blendor containing 125 ml of distilled water, 2.85 g (0.0125 mol) of 2,2-bis(4-hydroxyphenyl)propane, 1.1 g (0.0275 mol) of sodium hydroxide, and 1.2 g (0.007 mol) of tetraethylammonium chloride was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of 2,6(bischloroformyl)-9-oxabicyclo-[3.3.1]nonane (V) in 75 ml of ethylene dichloride. The reaction mixture was stirred 5 min and poured into 1 l. of methanol. The precipitated polymer was washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 5.3 g of polymer with η_{inh} 1.06 and PMT of 280°.

Preparation of Polycarbonate (X). To a Waring Blendor containing 3.53 g (0.0125 mol) of V and 125 ml of tetrahydrofuran was added, with stirring, a solution of 3.12 g (0.125 mol) of bis(4-hydroxyphenyl) sulfone, 2.65 g (0.0275 mol) of sodium carbonate, and 75 ml of water. The reaction mixture was stirred for 5 min and poured into 1 l. of methanol. The precipitated polymer was washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 5.1 g of polymer with η_{inh} 0.97 and PMT of 290°.

Preparation of XI. To a small polymer tube was charged 4.38 g (0.011 mol) of VI, 1.10 g (0.010 mol) of resorcinol, and 0.005 g of triphenylphosphene. The tube was placed in a refluxing ethylene glycol bath (198°), and the reaction lowed to proceed overnight. The solid product obtained was ground in a mortar and pestle, returned to the polymer tube, and polymerization finished off at 220° under 1 mm

pressure for 18 hr. Polymer, PMT of 270°, with η_{inh} 0.50, was obtained.

Preparation of XII. A small polymer tube containing 4.38 g (0.011 mol) of VI, 1.10 g (0.010 mol) of hydroquinone, and 0.005 g of triphenylphosphene was treated as in the previous example. Polymer, PMT of 310°, with η_{inh} 0.53, was obtained.

Preparation of XIII. A small polymer tube containing 4.38 g (0.11 mol) of VI, 1.58 g (0.01 mol) of III, and 0.005 g of triphenylphosphene was treated as in a previous experiment. Polymer, PMT 256°, with η_{inh} 0.70, was obtained.

Preparation of XIV. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, 2.63 g (0.0125 mol) of bis(4-aminocyclohexyl)methane (53% *trans,trans* isomer), and 25 ml of ethylene dichloride was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 50 ml of ethylene dichloride. The reaction mixture was stirred 5 min and poured into hot water. The ethylene dichloride was boiled off and the precipitated polymer washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 4.8 g of polymer with η_{inh} of 1.80 and a PMT of 312°.

Preparation of XV. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, 2.63 g (0.0125 mol) of bis(4-aminocyclohexyl)methane (70% *trans,trans* isomer) and 25 ml of ethylene dichloride was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 50 ml of ethylene dichloride. The reaction mixture was stirred for 5 min and poured into hot water. The ethylene dichloride was boiled off and the precipitated polymer was washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. The yield was 4.8 g of polymer with η_{inh} 1.66 and a PMT of 39°.

Preparation of XVI. To a Waring Blendor containing 125 ml of water, 2.65 g (0.0275 mol) of sodium carbonate, and 1.08 g (0.0125 mol) of piperazine was added, with rapid stirring, a solution of 3.53 g (0.0125 mol) of V in 75 ml of ethylene dichloride. After stirring for 5 min, the reaction mixture was poured into water and the precipitated polymer washed three times with water, three times with methanol, and dried at 70° *in vacuo* overnight. Yield was 3.6 g of polymer with η_{inh} 2.25 and a PMT of 388°.

Preparation of XVII. A solution of 2.37 g (0.015 mol) of III and 3.75 g of bis(4-isocyanotophenyl)methane in 20 ml of dry dimethyl sulfoxide was heated for 4 hr. The solution was poured into water, and the precipitated polymer washed three times with water and dried at 70° *in vacuo* overnight. The yield was 5.9 g of polymer with η_{inh} 0.7 and a PMT of 285°.

Preparation of XVIII, XIX, XX, and XXI. The above polymers were prepared by the catalyst and procedure used for the preparation of XIII.

Infrared spectra were recorded on a Perkin-Elmer Model 21 with a sodium chloride prism, thin films being obtained by melting samples on the prism. The pertinent bands for the previously mentioned compounds, between 9 and 10 μ, are given in Table IV.

On the Shape of the Intramolecular Scattering Function for Chain Molecules in Good and Poor Solvents[1,2]

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ABSTRACT: A light-scattering study of the intramolecular scattering function was conducted using very narrow fractions of polystyrene and poly(dimethylsiloxane) in both Θ solvents and good solvents. By combining the angular and the wavelength dependence of the data it was possible to study the scattering function over a wide range of values and to make meaningful comparison of the results with the theoretical equations of Debye and Isihara for Θ solvents, and of Ptitsyn and others for good solvents. For the Θ systems it was found that the equations of Debye and Isihara, which were found by numerical calculations to be experimentally indistinguishable for cases of practical interest, accounted well for the results. On the other hand, for good solvents the Ptitsyn equation overestimated the influence of the excluded volume effects on the scattering function. In fact, as long as the molecular weight of the polymer was less than a few million, the Debye equation fit the results very well. For molecular weights greater than a few million it was necessary to use the Ptitsyn function to fit the data, but with an excluded volume parameter ϵ smaller than the *a priori* value calculated from the Mark–Houwink viscosity–molecular weight exponent.

Debye's[4] classical equation for $P(\theta)$, the intramolecular scattering function for chain molecules, has been criticized from two different points of view. Since 1957, one group of workers[5-9] has maintained that his equation should be valid at the Θ condition, but not in good solvent systems, where non-Gaussian chain statistics become operative due to long-range intramolecular interactions. A more recent criticism has

(1) Taken in part from a thesis presented by T. E. S. in partial fulfillment of the requirements for the Ph.D. degree, Georgia Institute of Technology, 1967.

(2) Presented in part at the 153d National Meeting of the American Chemical Society, Division of Polymer Chemistry, Miami Beach, Fla., April 1967; *cf. Polym. Preprints*, **8**, 616 (1967).

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