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SYNTHESIS AND CHARACTERIZATION OF THE POLYESTER MADE FROM 1,1′-BIS(3-METHYL-4-HYDROXYPHENYL)CYCLOHEXANE WITH ISOPHTHALIC/TEREPHTHALIC ACIDS

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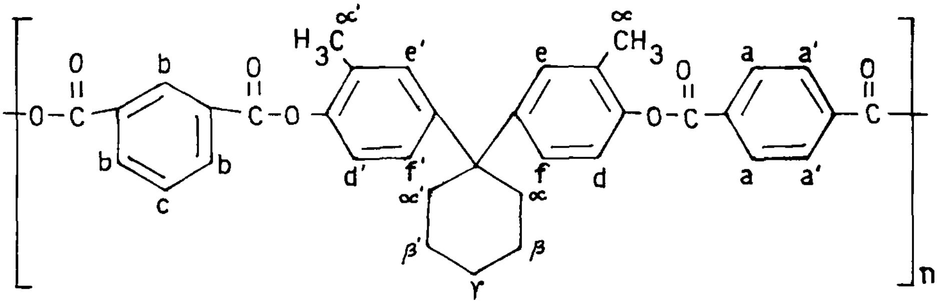
ABSTRACT

Condensation polymers of 1,1′-bis(3-methyl-4-hydroxyphenyl)-cyclohexane with isophthalic/terephthalic acids (PMeBCIT) have been synthesized by conventional interfacial polycondensation of 1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane with isophthaloyl and terephthaloyl chlorides (1:1) using water/1,2-dichloroethane as interphase, alkali as acid acceptor, and sodium laurylsulfate as emulsifier. The fractions were characterized by viscometry and gel permeation chromatography. The unfractionated PMeBCIT was characterized by IR and NMR spectra. Thermal and mechanical properties were also investigated. The PMeBCIT has excellent properties, such as good solubility range and flexibility, as well as good thermal, mechanical, and dielectric properties.

INTRODUCTION

Copolyesters and polyarylates [1-9] are well known as films, fibers, coatings, etc. with good heat resistance, good electrical properties, absorption resistance, high melting point, high softening point, and improved solubility. The presence of cardo (Latin, meaning loop) groups in the polymer backbone chain endows them with very specific properties: enhanced thermal stability together with excellent solubility and high flexibility [9].

The present communication encompasses the synthesis and characterization of poly[1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane isophthalate-terephthalate] (PMeBCIT) (I):



EXPERIMENTAL

Materials

The chemicals used were of laboratory grade and were purified prior to use by literature methods [10]. 1,1'-Bis(3-methyl-4-hydroxyphenyl)cyclohexane (MeBC) and the acid chlorides of isophthalic and terephthalic acids were synthesized according to reported methods [11, 12].

Polymer Synthesis

To a cooled and clear solution of MeBC (2.96 g, 0.01 mol) in 0.02 *M* NaOH (100 mL), sodium laurylsulfate (0.6 g) was added with constant vigorous agitation. A solution of isophthaloyl and terephthaloyl chlorides (1.01 g, 0.005 mol each) in 1,2-dichloroethane (30 mL) was added rapidly and the emulsion was stirred vigorously at 5°C for 5 h. The organic layer was separated and run into methanol to precipitate the polymeric product. The product was filtered, washed with water and methanol, and dried. It was further purified by dissolving in chloroform and precipitating with methanol. The yield was 97%.

The polymer, poly[1,1′-bis(3-methyl-4-hydroxyphenyl)cyclohexane isophthalate-terephthalate] (I), here designated as PMeBCIT, is soluble in benzene, chlorobenzene, 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, chloroform, dichloromethane, dioxane, toluene, etc. The polymer forms tough and transparent films from chloroform solution.

PMeBCIT was fractionated by fractional precipitation with 1,2-dichloroethane as solvent and absolute alcohol as precipitant at 30 ± 0.2°C. A standard procedure was used, and 9 fractions were obtained.

Measurements

Thin and thick films of PMeBCIT were prepared according to the literature method [13]. The IR spectrum was scanned on a Shimadzu DR-1, 435 IR spectrometer. The mechanical testing, dielectrical properties determinations, and hardness measurements were carried out on a Precision tensile testing machine R.T.6, Break-Down Tester B.D.V.-5, and Universal Research microscope CZ NU 2, respectively. Thermal measurements were carried out on a Shimadzu DTC-30H differential thermal analyzer. The NMR spectrum was scanned in $CDCl_3$ on a Varian XL-100A 100.1 MHz NMR spectrometer with TMS as internal standard. The viscometric measurements were carried out with an Ubbelohde-type suspended-level viscometer, and the gel permeation chromatographic measurements were carried out on a Waters Associates GPC-200, equipped with a set of four columns containing Styragel (10^6, 10^5, 10^4, and 20^3 Å) at 25°C, with chloroform as solvent.

RESULTS AND DISCUSSION

The important absorption bands (cm^{-1}) observed in PMeBCIT are 1740 (C=O str), 1290 (C−O str), 1610 (O=C−O asym str), 1400 (O=C−O sym str), 860 and 800(C−H o-o-p def.) besides the normal modes of vibration of the alkane, alicyclic, and aromatic groups. The NMR spectrum shows five distinct signals, viz., two singlets at 2.25 and 1.58 ppm are due to $-CH_3$ and $-CH_2$ protons (α) and β + γ protons of the cyclohexyl ring, respectively. The multiplets at 7.08–7.32 (77 mm high) and 8.34–8.58 ppm (47 mm high) are due to nine protons (six of the bisphenol and three of the isophthaloyl moiety) and five protons (four of the terephthaloyl and one of the isophthaloyl moiety) of the aromatic rings.

The composition of the PMeBCIT was determined by the following relation:

$$h_I/h_T = (3h_1 + 5h_2)/12h_1,$$

where h_I and h_T are the contributions to the peak height due to isophthaloyl and terephthaloyl groups; h_1 is the total peak height due to one terephthaloyl and one isophthaloyl protons; and h_2 is the total peak height due to three isophthaloyl and six phenolic protons.

The ratio h_I/h_T is found to be 0.966, i.e., approximately equal to unity. Thus the composition of isophthaloyl to terephthaloyl in PMeBCIT is 1:1, and the IR in conjunction with NMR data proves Structure I.

The DTA thermograms showed a glass-transition temperature at about 220°C and a decomposition temperature at about 440–460°C, respectively, in both air and nitrogen.

A 1-mm PMeBCIT film has 312 kg/cm^2 tensile strength, 1040 kg/cm^2, Young's modulus, 30% elongation at break, and 4.8 kV dielectric breakdown strength. There is not much variation in hardness with changing the load (Table 1). Thus, PMeBCIT has good thermal, mechanical, and dielectric properties.

TABLE 1. Microhardness of PMeBCIT Film at Different Loads[a]

Load, g	Hardness, kg/mm^2
28.6	14.2
36.2	13.3
48.6	13.3
67.6	14.2
82.2	13.9
93.2	13.5

[a] Time of indentation: 30 s. Room temperature.

Viscosity-Molecular Weight Relations

Viscosity data in various solvents are given in Table 2, GPC data in Table 3.

The experimental [η] is correlated with the $\bar{M}_w$ by the empirical Mark-Houwink-Kuhn-Sakurada (MHKS) relationship [15]. Linear regression analysis of the experimental data yields the following relations at 30°C for [η] in dL/g:

$$
\begin{aligned}
[\eta] &= 3.34 \times 10^{-4}\,\bar{M}_w^{0.67} \text{ (chloroform)}\\
&= 2.69 \times 10^{-4}\,\bar{M}_w^{0.67} \text{ (chlorobenzene)}\\
&= 4.52 \times 10^{-4}\,\bar{M}_w^{0.64} \text{ (1,2-dichloroethane)}\\
&= 1.61 \times 10^{-4}\,\bar{M}_w^{0.76} \text{ (1,1,2,2-tetrachloroethane)}\\
&= 0.72 \times 10^{-4}\,\bar{M}_w^{0.35} \text{ (toluene)}
\end{aligned}
$$

See Fig. 1.

TABLE 2. Intrinsic Viscosity [η] and Huggins Constant [14] for PMeBCIT Fraction at 30°C[a,b]

Fraction number	TCE		CF		CB		DCE		T	
	[η]	*k*	[η]	*k*	[η]	*k*	[η]	*k*	[η]	*k*
F-1	1.13	0.50	0.94	0.57	0.92	0.36	0.86	0.60	0.58	0.45
F-2	1.03	0.46	0.84	0.30	0.78	0.10	0.74	0.17	0.48	0.27
F-3	1.00	0.48	0.65	0.27	0.64	0.10	0.68	0.15	0.40	0.27
F-4	0.77	0.25	0.58	0.23	0.48	—	0.58	0.16	0.36	0.23
F-5	0.61	0.12	0.47	0.21	0.44	—	0.50	0.10	0.32	0.13
F-6	0.50	0.39	0.35	0.15	0.26	0.16	0.38	0.10	0.30	0.10
F-7	0.40	—	0.32	0.10	0.26	0.13	0.30	0.11	0.26	0.14
F-8	0.32	0.15	0.27	—	0.20	0.11	0.24	0.11	0.22	0.13
F-9	0.28	0.10	0.22	—	0.12	—	0.12	0.11	—	—

[a] In dL/g.

[b] TCE = 1,1,2,2-tetrachloroethane, DCE = 1,2-dichloroethane, CF = chloroform, T = toluene, CB = chlorobenzene.

TABLE 3. Molecular Weight and Molecular Weight Distribution Obtained from GPC Data in Chloroform at 30°C[a]

Fraction number	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
F-1	22.3	12.7	1.8
F-2	17.4	9.3	1.9
F-3	11.4	8.0	1.4
F-4	6.2	5.4	1.2
F-5	5.0	3.8	1.3
F-6	3.6	2.9	1.2
F-7	3.0	2.5	1.2
F-8	2.0	1.7	1.2
UNF[b]	10.0	4.5	2.2

[a] After heterogeneity correction.

[b] Unfractionated PMeBCIT.

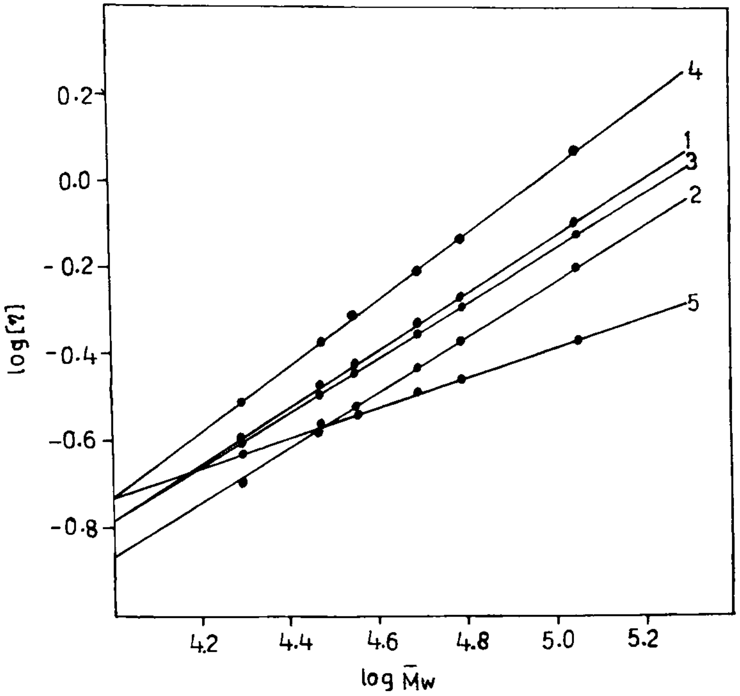


FIG. 1. Dependence of the intrinsic viscosity of PMeBCIT at 30°C in chloroform on the weight-average molecular weight. (1) Chloroform, (2) chlorobenzene, (3) 1,2-dichloroethane, (4) 1,1,2,2-tetrachloroethane, and (5) toluene.

TABLE 4. The Unperturbed Dimensions (K) and Polymer–Solvent Interaction Parameter (B) for PMeBCIT in Various Solvents at 30°C[a]

	$K \times 10^3$, dL·mol$^{1/2}$·g$^{-3/2}$				$B \times 10^{27}$, cm^3			
Solvent	SFB	FOP	KSR	FFS	SFB	FOP	KSR	FFS
TCE	1.69	1.36	1.96	1.64	4.91	2.67	2.19	1.71
CF	1.16	1.36	1.25	1.35	4.80	1.84	2.62	1.17
CB	1.22	1.00	1.36	1.01	1.95	2.51	0.96	2.22
DCE	1.67	1.05	0.77	1.71	1.54	1.96	4.73	4.80
T	1.66	1.80	1.89	1.78	−1.51	−0.83	−1.13	−0.31

[a] TCE = 1,1,2,2-tetrachloroethane, CF = chloroform, CB = chlorobenzene, DCE = 1,2-dichloroethane, T = toluene.

The exponent in the MHKS equation lies in the range 0.5–0.8 generally observed for polymers that are flexible in solution, while exponents below 0.5 indicate tightly coiled configurations of the macromolecular chains [16].

On the basis of the [η] in Table 2, the order of thermodynamic "goodness" of the solvents is TCE > CF > CB > DCE > T. The MHKS exponent is maximum in TCE and minimum in toluene.

Several methods [17–23] have been proposed for the estimation of the unperturbed dimensions of polymeric chains from the viscosity data in nontheta solvents. The methods, based on the current two-parameter theories of excluded volume [17], involve extrapolation of the appropriate viscosity function to zero MW. Graphical methods based on Stockmayer-Fixman-Burchard (SFB) [17–19], Kurata, Stockmayer, and Roig (KSR) [20], first-order perturbation (FOP) [17, 23], and Flory, Fox, and Schaefgen (FFS) [21, 22] were employed to estimate the unperturbed dimensions K_θ and the solvent–polymer interaction parameter B (see Table 4). None of the theories yields the same K for all the solvents although, according to the concept of the theta state, the unperturbed dimensions should be independent of the nature of the solvent. The observed solvent dependence of the unperturbed dimensions of PMeBCIT is attributed to the so-called solvent effects. Such effects are well documented [24–30], and it has been suggested that they are caused by a dependence of the chain conformational energy on the solvent dielectric constant [31] or by direct interaction of the solvent with the polymer [32, 33].

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