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Properties of Poly(*p*-phenylene terephthalates) Prepared from 2-Nitro- and 2-Bromoterephthalic Acids and Substituted Hydroquinones[†]

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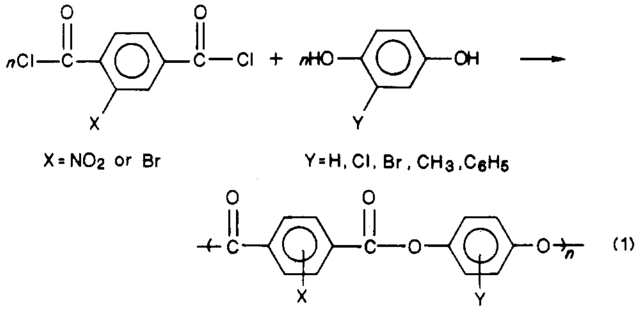
ABSTRACT: Two series of aromatic polyesters were prepared from 2-nitro- and 2-bromoterephthalic acids and substutited hydroquinones. All of the polymers, with the exception of those with NO_2/CH_3, NO_2/C_6H_5, and Br/CH_3, were thermotropic nematogens. The NO_2/CH_3 and Br/CH_3 polymers were smectogens, while the NO_2/C_6H_5 composition was amorphous and non-liquid crystalline. In general, annealing enhanced the degree of crystallinity noticeably, as indicated by DSC and X-ray diffractometry, with the only exception being the NO_2/C_6H_5 composition, which did not crystallize even after prolonged thermal treatment. The crystal–mesophase transition temperature, T_m, ranged from 180 to 365 °C depending on the size and number of substituents. The glass transition temperature, T_g, of the polymers also was dependent on the number and size of substituents on the repeating units and ranged from 60 to 110 °C. DSC and TGA studies revealed that the thermal stability of polymers derived from 2-nitroterephthalic acid was significantly poorer than that of polymers prepared from 2-bromoterephthalic acid. The nematic–isotropic transition temperatures, T_i, could be determined by DSC only for polyesters derived from 2-bromoterephthalic acid, due to the poor thermal stability of 2-nitroterephthaloyl polymers.

Introduction

In recent years thermotropic, main-chain poly- and copolyesters have attracted a great deal of interest due to the possibility of melt processing them from their nematic melts into fibers or plastics having high strength.[1-6] The two representative aromatic polyesters, poly(*p*-hydroxybenzoic acid) and poly(*p*-phenylene terephthalate), however, have melting temperatures too high for melt processing. This has led to the synthesis of many aromatic polyesters with nonlinear structural segments or with various substituents, random copolyesters and segmented polyesters having a rigid and a flexible spacer in the repeating unit as a means of reducing the melting temperatures, T_m, of the resulting compositions to a processable range.

Interest is growing also in the structure–property relationship of these thermotropic polyesters, and quite a few systematic studies have been published by us[4-6] and others.[1-3] An early British patent by Goodman et al.[7] described poly(*p*-phenylene terephthalates) with substituents, such as methyl, methoxy, or halogen on one or both benzene rings of the repeating unit. The authors, however, did not appear to realize that these polyesters were thermotropic compositions. While we were conducting this investigation, Krigbaum, Hakemi, and Kotek[8] investigated various mono- and disubstituted poly(*p*-phenylene terephthalates) and found that disubstituted polyesters had T_ms of 205–235 °C and T_is of 230–370 °C depending on the position and size of subsituents.

In this study we have synthesized two series of poly(*p*-phenylene terephthalates) from 2-nitro- and 2-bromoterephthalic acids and hydroquinones with substituents, such as hydrogen, chlorine, bromine, methyl, or phenyl, (see eq 1), and we have determined their crystalline, liquid crystalline, and thermal properties. The three compositions derived from 2-bromoterephthalic acid and hydroquinone with Y = H, Cl and C_6H_5 were described previously by Krigbaum et al.[8] Our results for these are included in this report for comparison. For simplicity we have described the polymers by the symbol X/Y, where X and Y stand for the substituents on the terephthalic acid and hydroquinone units, respectively.



(1)

polymer X/Y

Results and Discussion

General Properties and Glass and Melting Transitions. Solution viscosity numbers and thermal transition temperatures such as glass transition temperature (T_g) and melting temperature (T_m) of the polymers are shown in Table I. Both interfacial and solution polymerization methods were used for all of the compositions, but only the data for the sample with the higher molecular weight are included in the table.

The polymers were soluble either in a phenol/1,1,2,2-tetrachloroethane (TCE), phenol/*p*-chlorophenol/TCE, or *p*-nitrophenol/*p*-chlorophenol/TCE mixture or in *p*-chlorophenol, depending on their structure. Polymers with NO_2/Br and Br/Cl substituents were soluble only in strong acids, such as H_2SO_4, CF_3SO_3H, etc., but solution was accompanied by an appreciable degree of decomposition. Since the solubilities of all the polymers were relatively low, even in those solvents designated, a concentration of 0.1 g/dL was employed for the measurement of solution

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Table I
General Properties and Transition Temperatures of Polyesters

		as-polymerized samples							annealed samples							
polymer	prep method[a]	η_{inh}[b]	T_g, °C	T_{k-k}, °C	T_m, °C	ΔH_t,[c] kJ/mol	T_i, °C	DC,[d] %	T_a,[e] °C	η_{inh}[b]	T_g, °C	T_{k-k}, °C	T_m, °C	ΔH_t,[c] kJ/mol	T_i, °C	DC,[d] %
NO_2/H	I	0.77	69	194	218	1.0		1.5	210	ins	67	191	228	2.2		54
NO_2/Cl	S	0.63	75	199	211	1.0		3	185	0.64	74	207	213	4.0		27
NO_2/Br	I	ins	81						130	ins	86		143	0.6		*f*
									185	ins	84		222	1.9		*f*
									210	ins	89		237	1.8		*f*
									220	ins	91		237	1.9		5
NO_2/CH_3	I	0.49	80	186	205	0.8		6	180	ins	84		213	1.8		18
NO_2/C_6H_5	I	0.27	101						125	0.28	109					
									150	0.27	107					
									170	0.27	107					
Br/H	I	0.29		288, 310	362	6.9	476	6	270	ins		291, 305	391	6.4	499	39
Br/Cl	I	ins	112	199	228	1.5	379	2	185	ins	111	199	248	4.9	382	14
Br/Br	S	0.66	80	191	234	7.6	416	1.5	185	ins	81	191, 206	234	10.0	413	*f*
									220	ins	80	187	237	8.9	415	18
Br/CH_3	S	0.43	60	146	174	1.2	406	8	130	0.43	67	148, 154	175	2.5	401	*f*
									150	0.43	61	159	179	2.2	401	22
Br/C_6H_5	I	0.44	86	160	181	0.6	312	7	150	0.44	85		187	0.7	314	9

[a] I designates interfacial and S solution polymerization. [b] Inherent viscosities of the NO_2/CH_3, NO_2/C_6H_5, and $Br/_6H_5$ polymers measured by using a 0.1 g/100 mL solution in a phenol/TCE = 60/40 (w/w) mixture. A mixed solvent of phenol/*p*-chlorophenol/TCE = 25/40/35 (w/w/w) was used for the NO_2/Cl and Br/CH_3 polymers and *p*-chlorophenol for the Br/H and Br/Br polymers. NO_2/H was soluble in a mixed solvent of *p*-nitrophenol/*p*-chlorophenol/TCE = 6/50/44 (w/w/w). Proper organic solvents could not be found for the NO_2/Br and Br/Cl polymers. [c] Total enthalpy changes for crystal–crystal and crystal–nematic transitions. [d] Degree of crystallinity. [e] Annealing temperature. Samples were annealed or 15 h at T_a. [f] Not available.

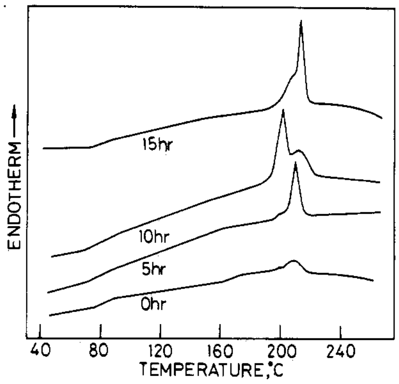


Figure 1. DSC thermograms of the NO_2/Cl polymer before and after annealing.

viscosities. The solution viscosity numbers were reasonably high with the exception of those for the NO_2/C_6H_5 and Br/H polymers. In general, the polymer samples annealed at higher temperatures (>ca. 185 °C) became insoluble, probably due to their increased molecular weight and enhanced degree of crystallinity (see Table I); this will be discussed later. Solution viscosity numbers of the polymers annealed at lower temperatures, however, remained unchanged from as-polymerized samples (Table I), indicating very little change in the molecular weight.

The T_gs of the polymers, both "as-polymerized" or annealed, could be clearly positioned in the heating curves of their DSC (e.g., Figures 1 and 2). The only exception was the Br/H polymer, whose T_g could not be determined from either an as-polymerized or annealed sample. Krigbaum et al.[8] also reported the same experience with this composition. The T_gs of the polymers were in the temperature range 60–110 °C. These values seem to be somewhat lower than those (108–122 °C) reported by Krigbaum et al. for similar polyesters. For example, they reported a T_g of 120 °C for the Br/C_6H_5 polymer, while we found a T_g value of 86 °C for the same composition. The reason for such a discrepancy appears to have originated from the lower molecular weights of the present polymers. Annealing did not alter the T_gs of the polyesters to any significant extent.

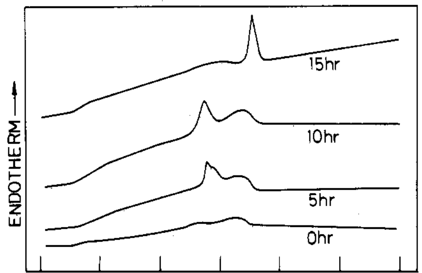


Figure 2. DSC thermograms of the Br/CH_3 polymer before and after annealing.

Since the van der Waals radius of CH_3 is about the same as that for Br, polymers with these substituents would be expected to have about the same T_gs. This was observed for the NO_2/Br and NO_2/CH_3 polymers. The Br/CH_3 composition, however, exhibited a particularly low T_g, 60 °C, compared with that of Br/Br, 80 °C. The lower T_g of the former appears to be due to its lower MW. The relatively high T_g values, 101 or 107 °C depending on thermal history, of the NO_2/C_6H_5 polymer compared with those of other compositions in the same NO_2 series must be due to the reduced rotational freedom resulting from the steric hindrance exerted by the phenyl substituent. The same tendency also was observed for the Br polymer series but was less pronounced.

All of the as-polymerized samples, with the exception of monosubstituted NO_2/H and Br/H, showed very weak DSC melting endotherms; these became much more distinct upon annealing (Figures 1 and 2). The NO_2/C_6H_5 polymer was the only exception in that it did not exhibit a melting transition either for the as-polymerized or for the annealed sample, implying its intrinsic amorphous nature. This compares very well with the amorphous nature of the C_6H_5/C_6H_5 polyester as reported earlier.[8] It is evident that a combination of the large size and the possible positional isomerism of the phenyl substituents on the two rings prevents crystallization of the polymer. The melting points of the semicrystalline polymers ranged from 180 to 360 °C for as-polymerized samples. The T_ms

Table II
Dependence of Transition Temperatures and Degree of Crystallinity on Annealing Time

polymer	annealing time, h	η_{inh}	T_g, °C	T_{k-k}, °C	T_m, °C	ΔH_t, kJ/mol	T_i, °C	DC, %
NO_2/Cl[a]	0	0.63	75	179	211	1.0		3
	5	*c*	74	199	211	1.8		*c*
	10	*c*	74	196	209	3.3		*c*
	15	0.64	74	207	213	4.0		27
Br/CH_3[b]	0	0.43	60	146	174	1.2	406	8
	5	*c*	63	149, 154	174	1.8	401	*c*
	10	*c*	62	146	175	2.3	401	*c*
	15	0.43	61	159	179	2.2	401	22

[a] Samples were annealed at 185 °C. [b] Samples were annealed at 150 °C. [c] Not available.

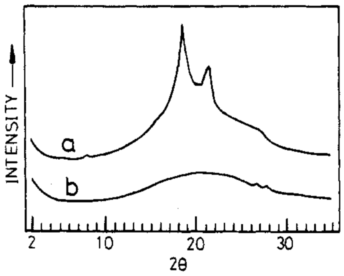


Figure 3. X-ray diffractograms of the NO_2/H polymer: (a) after and (b) before annealing.

of disubstituted polymers in the Br series are considerably lower than that of Br/H. On the other hand, the differences in T_ms between the monosubstituted (T_m, 218 °C) and disubstituted NO_2 polymers (205–210 °C) are much less pronounced. This can be ascribed to the fact that the size of the NO_2 substituent existing on one of the rings is large enough to accommodate a second substituent on the other ring. Thus the introduction of the second substituent resulted in only a slight reduction in T_m. The fairly low T_g, 69 °C, of the NO_2/H polymer indeed suggests the presence of large free volume caused by the substituent.

Most of the polymers showed crystal–crystal transition(s) (T_{k-k} in Table I) before melting, indicating that they are polymorphous. Annealing, in general, favored the formation of higher temperature polymorphs, as observed by the position and the size of the transition peaks on the DSC curves (Table I and Figures 1 and 2). A detailed discussion of the thermal treatment of the polymers follows in the next section.

The T_gs and T_ms of the disubstituted polymers are much lower than that of poly(p-phenylene terephthalate), reported as 267[9] and 600 °C,[1] respectively. A combination of increased internal mobility by the substituent on the phenyls and possible random variations along the chain of the substituent positions must have caused these reductions in T_gs and in T_ms. It should be noted that the values of the ratio in degrees kelvin of T_g/T_m of the present polymers range from about 0.5 to 0.8, similar to that of other polyesters. The T_m value of the Br/C_6H_5 polymer is significantly lower than that reported by Krigbaum et al.,[8] probably for the same reason given for its low T_g observed, i.e., lower molecular weight and different thermal history.

Crystallization. As mentioned above, most of the as-polymerized samples not only showed very weak or no melting endotherms in the heating curves of the DSC curves but also exhibited very low crystalline scattering intensities in X-ray diffractograms (Figures 3 and 4). This suggests that the crystallization rate of the polymers was so slow that they crystallized, if at all, only to a minor extent during polymerization and during the heating period of the DSC runs. The two as-polymerized polymers with NO_2/Br and NO_2/C_6H_5, in particular, appeared to be amorphous according to DSC and X-ray analyses. The remaining polymers, however, even as-polymerized samples, exhibited weak, but definite crystal–crystal and melting transitions (see Table I and Figures 1 and 2). In order to see if the polymers could be further crystallized, we annealed the polymers for 15 h, generally at the temperature where the initial slope change in the DSC curve was observed for the first crystal–crystal transition peak. Table I contains the annealing temperature, T_a, of each polymer, as well as the approximate degree of crystallinity of each polymer before and after annealing. The degree of crystallinity was estimated from the crystalline and the amorphous reflection areas in the X-ray diffractograms. Figures 1 and 2 show how the DSC thermograms of the NO_2/Cl and Br/CH_3 polymers changed with annealing time. With the former, the relative area for the transition of the highest temperature polymorph (T_m = 213 °C) and the total transition area grew with annealing time. With the latter, during the annealing time of 10 h, the endotherm for the lowest temperature polymorph (146 °C) initially increased and later disappeared, while that of the higher temperature polymorph (175 °C) grew much more intense. Here again the total endothermic area grew with thermal treatment.

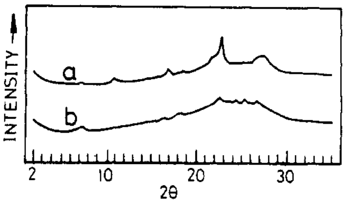
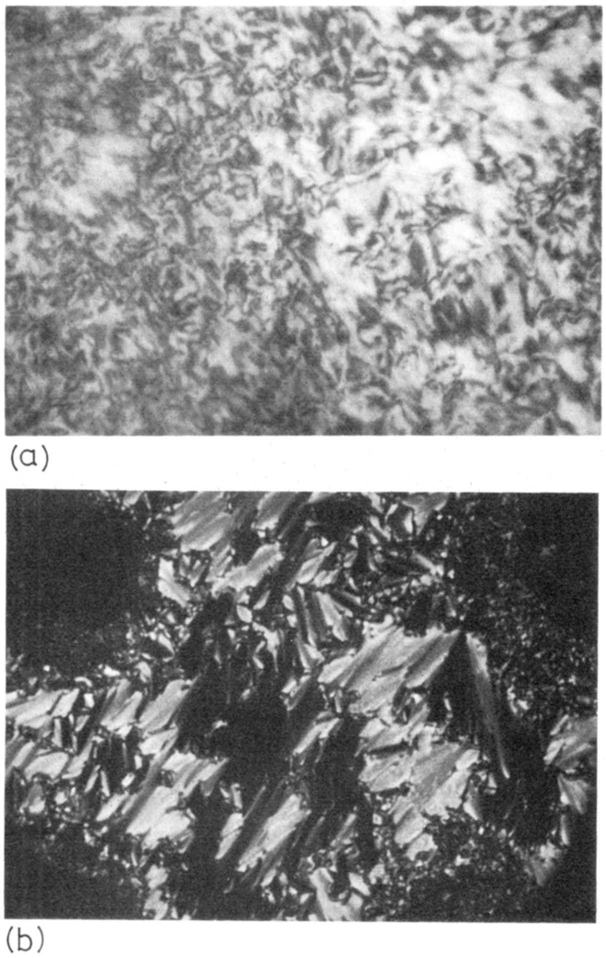


Figure 4. X-ray diffractograms of the Br/H polymer: (a) after and (b) before annealing.

Table II shows how the transition temperatures, T_{k-k}s, of different crystalline polymorphs and T_ms of the NO_2/Cl and Br/CH_3 polymers changed with annealing time. This table also gives the values of total transition enthalpy, ΔH_t, involving crystalline states, i.e., ΔH for all of the crystal–crystal and melting transitions. For the NO_2/Cl composition, ΔH_t steadily increased with annealing time, while for the Br/CH_3 composition, it initially increased and then leveled off after an annealing time of 10 h. Table I relates T_{k-k}, T_m, and ΔH_t to annealing temperature for the NO_2/Br, Br/Br and Br/CH_3 polymers. As mentioned earlier, the NO_2/Br composition, as-polymerized, was amorphous and became crystalline only after annealing. When it was annealed at 130 °C for 15 h, it showed only one weak and broad melting endotherm around 143 °C, with the heat of melting, ΔH_m, calculated to be only 0.6 kJ/mol. The composition, however, showed T_ms of 222 and 237 °C when annealed at 185 and 210 °C, respectively. The heat of melting, ΔH_m (1.9 kJ/(mol repeat unit)), i.e., the area of melting endotherm on the DSC curves, remained more or less constant when its T_a was higher than 185 °C (Table I). Certainly, the low-temperature crystal


(a)

(b)

Figure 5. Photomicrographs of (a) NO_2/Cl (255 °C) and (b) Br/CH_3 (298 °C) polymer melts (magnification 65×).

form whose T_m was 143 °C had completely disappeared at higher annealing temperatures, and a new crystalline form was attained.

Figures 3 and 4 present X-ray diffractograms of the NO_2/H and Br/H polymers before and after annealing. Crystalline reflection, and thus the degree of crystallinity, certainly increased with annealing (see Table I). All of those observations tell us that annealing increases the degree of crystallinity of the polymers and that polymorph formation is dependent on the thermal history of the samples. It was also observed that, in general, X-ray patterns for the NO_2 polymers improved to a greater extent on annealing when compared with those of the Br series.

For all of the polymers, X-ray reflections of less than 5 Å were observed; these correspond to interchain spacings in the lateral packing of the polymer molecules.[4,8] Spacings of about 12 Å, which correspond to regular packing along the chain direction, were observed for all but three annealed NO_2/Br, NO_2/C_6H_5, and Br/Br polymers. This observation suggests that a regular arrangement of molecules is possible along the chain direction despite the expected random positional variation of substituents on the benzene rings.[8] The NO_2/Br and Br/Br polymers were unique in that they revealed reflections at 21–22 Å with very low intensities, but the 12 Å spacing was missing even for the annealed samples. Unfortunately, sufficient experimental data to present a better structural analysis is not yet available.

Nature and Transition of Mesophase. A typical photomicrograph of textures observed for the polymer melts observed through a polarizing microscope can be seen

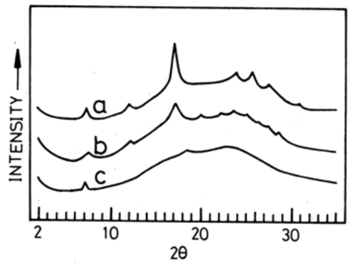


Figure 6. X-ray diffractograms of the NO_2/CH_3 polymer: (a) annealed, (b) as-polymerized, and (c) quenched samples.

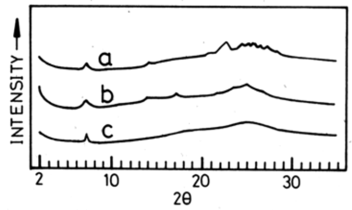


Figure 7. X-ray diffractograms of the Br/CH_3 polymer: (a) annealed, (b) as-polymerized, and (c) quenched samples.

in Figure 5a. It shows the so-called polished marble texture typical of nematogens. All of the present polymers, with the exception of the NO_2/C_6H_5, NO_2/CH_3, and Br/CH_3 compositions, formed only a nematic phase upon melting. The NO_2/C_6H_5 composition was found to be non-liquid crystalline. Strangely enough, the Br/CH_3 and NO_2/CH_3 polymers showed smectic textures (Figure 5b) on melting. Moreover, unlike other compositions, X-ray diffractograms of the quenched melts of these two polymers showed a sharp diffraction peak at 2θ of 7.2° corresponding to a spacing of about 13 Å (Figures 6 and 7), supporting their smectic nature. All other samples obtained by the quenching of polymer melts had only broad X-ray diffraction patterns centered around 4 Å, confirming their nematic nature. It is not yet clear why only these two compositions are capable of forming smectic mesophases. Krigbaum et al.[8] observed the coexistence of two nematic mesophases for the Br/C_6H_5 polymer. We, however, did not observe such a coexisting binary mesophase for the same composition. All of the sample formed a homogeneous mesophase.

Unfortunately, the thermal stability of the NO_2 series was so low that their nematic-to-isotropic transition temperatures, T_is, could not be determined by DSC analysis. On the other hand, fast heating (40 °C/min) of the Br series provided us with the isotropization DSC endotherms whose temperatures are shown in Table I. The values of T_is for Br/H (476 °C for the as-polymerized sample) and Br/Cl (379 °C for the as-polymerized sample) are comparable to those reported,[8] while the T_i value of the Br/C_6H_5 polymer (312 °C for the as-polymerized sample) in this study is significantly lower than the reported value, 376 °C,[8] probably due to the lower molecular weight of the present polymer. Annealing did not change the values of T_is; they remained the same as those for as-polymerized ones. One interesting phenomenon observed for the Br series is that the mesophase temperature range, ΔT, broadens from 110 to 227 °C as the size of X in Br/X increases. This indicates that the presence of substituents causes larger reductions in T_m than T_i. Nevertheless, the value of ΔT of the Br/C_6H_5 polymer was only 135 °C. We believe that the large size of the Br and C_6H_5 groups attached to the two benzene rings of the repeating unit results in a less extended conformation, which in turn reduces the axial ratio as compared with the other polymers. It is well-known that the reduction in axial ratio destabilizes the thermal stability of a mesophase.[10]

Table III
Results of DSC and Thermogravimetric Analyses[a]

polymer	T_D^i,[b] °C	T_D^2,[c] °C	T_D^{50}, °C	wt^R, %
NO_2/H	387 (293)	494	486	30
NO_2/Cl	352 (259)	480	495	31
NO_2/Br	340 (305)	474	503	16
NO_2/CH_3	325 (299)	510	528	17
NO_2/C_6H_5	322 (288)	500	561	45
Br/H	476 (470)		510	18
Br/Cl	339 (325)	456	495	28
Br/Br	472 (472)		504	21
Br/CH_3	442 (426)		491	39
Br/C_6H_5	395 (354)		526	43

[a] T_D^i and T_D^{50} are the temperatures where initial and 50% weight loss were observed. wt^R stands for the weight percent of residue remaining after the sample was heated to 600 °C. [b] The values in parenthese are the temperatures where initial decomposition endotherms on DSC appeared. [c] The temperature where the second weight loss begins. The polymers with T_D^2 exhibit two-stage weight loss on heating.

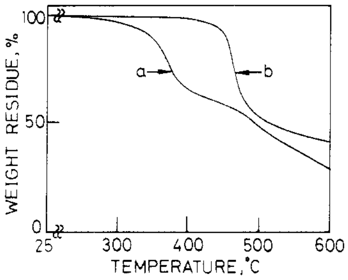


Figure 8. TGA thermograms of the (a) NO_2/Cl and (b) Br/CH_3 polymers.

Thermal Stability of the Polymers. The thermal stability of the polymers was studied by DSC and thermogravimetry. Table III summarizes the initial decomposition temperatures observed by DSC and TG analyses (T_D^i) and temperatures (T_D^{50}) where 50 wt % loss was observed. The table also presents weight residues, wt^R, at 600 °C. Figure 8 shows typical thermograms used in this study to obtain the data included in Table III. The NO_2 polymers exhibited two-stage weight losses on heating (Figure 8a) while most Br polymers showed only one-stage weight losses (Figure 8b). The Br/Cl polymer was an exception in that it revealed a two-stage weight loss. Further study is needed to explain these differences.

In general, the T_D^i values of the NO_2 series, as determined by DSC, were significantly lower than those of Br polymers. The presence of the NO_2 group appears to facilitate thermal fission of the polymer chains. This could be related to the fairly strong substituent effect of the NO_2 group, which increases the acidity of terephthalic acid and make the acid moiety more thermally labile. Steric hindrance could also reduce the thermal stability of the NO_2 series. Most of the polymers suffered 50 wt % loss when heated up to about 500 °C. The C_6H_5 polymers were the most efficient char formers, more than 40 wt % remained as residue when the sample was heated to 600 °C. This observation agrees with the well-documented phenomenon that increasing aromaticity of polymers is accompanied by an increase in char-forming capability.[11]

Conclusion

The following conclusions can be drawn from the present work:

1. All of the aromatic polyesters reported in this investigation were semicrystalline and thermotropic. The only exception was the NO_2/C_6H_5 polymer, which was found to be amorphous and non-liquid crystalline.

2. Almost all of the polysters formed nematic mesophases in melt; the two exceptions, the NO_2/CH_3 and Br/CH_3 polymers, formed smectic phases.

3. Transition behavior of the crystalline states of the polymers was highly dependent on the thermal history of the samples.

4. The T_ms of the polymers were reduced remarkably by the presence of substituents on each benzene rings of the repeating unit.

5. The thermal stability of the polymers derived from 2-nitroterephthalic acid was poorer than that of the compositions derived from 2-bromoterephthalic acid.

Experimental Section

Chemicals. 2-Nitroterephthalic acid (Fluka AG) and 2-bromoterephthalic acid (Aldrich Chemical Co.) were recrystallized from 80/20 (v/v) mixtures of water and ethanol. Hydroquinone (Junsei Chemical Co., Ltd.), 2-bromo-, and 2-chlorohydroquinones (Eastman Kodak Co.) were purified by vacuum sublimation. 2-Methyl- (Merck) and 2-phenylhydroquinones (Tokyo Kasei Kogyo Co., Ltd.) were used as received. Thionyl chloride (Junsei Chemical Co., Ltd.) was purified by refluxing with triphenyl phosphite followed by distillation. Other chemicals such as pyridine and 1,1,2,2-tetrachloroethane were purified by usual methods. The phenols used in the measurement of polymer solution viscosities were reagent grade and used without further purification. Benzyltriethylammonium chloride (Eastman Co.) was used as received.

Preparation of Polyesters. The polyesters was prepared by two methods, either by a solution polymerization method or by an interfacial method. For the solution method, 5 mmol of the dichloride, prepared either from 2-nitro- or 2-bromoterephthalic acid and thionyl chloride, was dissolved in 10 mL of 1,1,2,2-tetrachloroethane (TCE). This solution was added dropwise under a nitrogen atmosphere to a vigorously stirred solution of 5 mmol of a hydroquinone in 5 mL of TCE and 5 mL of pyridine. The reaction was allowed to proceed overnight at room temperature. Then the reaction mixture was heated to 60 °C and stirred for another hour before it was poured into ethanol. The precipitate was collected by filtration and washed with ethanol, dilute HCl, water, and methanol. The washed product was dried at 50 °C under vacuum.

In the interfacial method, 5 mmol of the dichloride of 2-nitro- or 2-bromoterephthalic acid was dissolved in 25 mL of TCE and vigorously stirred with a solution of an equimolar hydroquinone dissolved in 50 mL of water containing 0.6 g of NaOH and 1.0 g of benzyltriethylammonium chloride. The reaction mixture was mechanically stirred under a nitrogen atmosphere for 1 h at room temperature and then poured into acetone. The precipitate was collected by filtration and washed with ethanol, dilute HCl, water, and methanol. The polyesters thus obtained were dried at 50 °C under vacuum.

Characterization of Polymers. Inherent viscosities were determined at 45 °C using 0.1 g/100 mL solution in various solvents (Table I). The NO_2/Br and Br/Cl polymers were not soluble in phenolic solvents. They were soluble in strong acids such as H_2SO_4 and CF_3SO_3H but with significant degradation.

Transition temperatures and enthalpies were determined under a nitrogen atmosphere on a Du Pont 910 DSC at a heating rate of 10 °C/min. For the determination of isotropization temperatures (T_is), a faster heating rate, 40 °C/min, was employed. T_g was taken as the temperature at which the initial slope change was observed on the DSC thermogram, while the peak maxima positions were taken as other transition temperatures (T_m, $T_{k\text{-}k}$, and T_i). Indium, tin, and zinc served as references for calibration of the temperature scale and indium as a reference for enthalpy estimations of transitions. Thermogravimetrical measurements were conducted under a nitrogen atmosphere on a Mettler TA 3000 at a heating rate of 10 °C/min. Optical textures of polymer melts or quenched samples were observed on a polarizing microscope (Leitz, Ortholux) equipped with a Mettler FP-5 hot stage. X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa with nickel-filtered Cu Kα (λ = 1.542 Å) radiation. The scanning rate was 4 °/min. Specimens for X-ray analysis were prepared by pressing the polymer samples into films of ca.

0.5 mm. X-ray diffractograms of mesophases were obtained on samples obtained by quenching the polymer melts with a dry ice/acetone mixture. Annealing of polymers was conducted in a vacuum oven preheated to a desired temperature. Afterward, the annealed samples were slowly cooled to room temperature in the vacuum oven.

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Registry No. NO_2/H (copolymer), 107514-81-8; NO_2/H (SRU), 107556-07-0; NO_2/Cl (copolymer), 107514-82-9; NO_2/Cl (SRU), 107556-06-9; NO_2/Br (copolymer), 107514-83-0; NO_2/Br (SRU), 107556-04-7; NO_2/CH_3 (copolymer), 107514-84-1; NO_2/CH_3, 107556-09-2; NO_2/C_6H_5 (copolymer), 107514-85-2; NO_2/C_6H_5 (SRU), 107556-10-5; Br/H (copolymer), 107514-86-3; Br/H (SRU), 95978-14-6; Br/Cl (copolymer), 107514-87-4; Br/Cl (SRU), 95935-11-8; Br/Br (copolymer), 107514-88-5; Br/Br (SRU), 107556-05-8; Br/CH_3 (copolymer), 107514-89-6; Br/CH_3 (SRU), 107556-08-1; Br/C_6H_5 (copolymer), 107514-90-9; Br/C_6H_5 (SRU), 95935-16-3.

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Polymerization Behavior of 7,7-Dicyanoquinone Methide as an Acceptor Monomer

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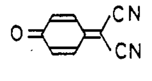
ABSTRACT: The electron affinity of 7,7-dicyanoquinone methide (CQM) was estimated by the charge-transfer band method to be 2.36 eV. It was found that CQM copolymerizes alternatingly with styrene (St) or *p*-methoxystyrene in benzene at 60 °C in the presence of α,α'-azobis(isobutyronitrile) (AIBN). Terpolymerizations of the CQM–maleic anhydride (MAnh)–St, CQM–*p*-chloranil (PCA)–St, and CQM–2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)–St systems in benzene at 60 °C in the presence of AIBN gave nearly alternating copolymers of CQM with St, CQM with St, and DDQ with St, respectively. These results of the terpolymerization plainly exhibit a relative polymerizability between a pair of acceptor monomers, suggesting that these four acceptor monomers may be arranged in the following order of relative polymerizability as acceptor monomer: MAnh < PCA < CQM < DDQ. This order, except for PCA, agrees with that of their electron-accepting character. In addition, several parameters of the reactivity of these acceptor monomers in their alternating copolymerizations with St were estimated by means of the π-electron LCAO MO method and were compared with experimental results, allowing us to suggest an idea about a rate-determining state in their alternating copolymerization.

Introduction

Previously it has been pointed out that highly electron-accepting quinodimethane and quinone compounds such as 7,7,8,8-tetracyanoquinodimethane (TCNQ),[1] 2,5,7,7,8,8-hexacyanoquinodimethane,[2] 11,11,12,12-tetracyanonaphthoquinodimethane (TNAP),[2] 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$),[3] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[4] 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane (TECQ),[5] and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)[6] are alternatingly and almost spontaneously copolymerizable as an acceptor monomer with donor monomers such as styrene (St) and vinyloxy compounds. In addition, *p*-benzoquinone bis(benzenesulfonimide) (QBS), with a highly electron-accepting property, was reported to exhibit a similar polymerization behavior.[7]

7,7-Dicyanoquinone methide (CQM), prepared originally by Hyatt,[8] was considered to be an interesting compound, intermediate between TCNQ and *p*-benzoquinone, because its chemical structure has oxygen and dicyanomethylene carbons at the exocyclic 7 and 8 positions, but its polymerization has not yet been studied.

In this work were investigated the polymerization behavior of CQM, its copolymerizations with St and *p*-methoxystyrene (MeOSt), and the terpolymerizations of St, CQM, and a second acceptor monomer such as maleic anhydride (MAnh), *p*-chloranil (PCA), and DDQ; its electron-accepting character was also measured. In addition, the reactivity of CQM, MAnh, PCA, and DDQ as acceptor monomers in their alternating copolymerizations with St was estimated by means of the π-electron linear combination atomic orbital (LCAO) molecular orbital (MO) method to get some idea about a rate-determining state in the alternating copolymerization.



CQM

Experimental Section

Materials. CQM was prepared from 1,4-cyclohexanedione and malononitrile according to the method of Hyatt.[8] MAnh was purified from the commercial product by subliming it in the presence of phosphorous pentoxide, and it was used immediately. Commercial DDQ was recrystallized from a mixture of benzene and chloroform (1/4 by volume) and then sublimed. PCA was purified by treating its benzene solution with calcium carbonate and then recrystallizing from benzene. MeOSt was prepared from anisole and acetyl chloride according to the method of Overberger