istence of the selection process is clearly confirmed by this experiment.

Concluding Remarks

From the results presented above it is concluded that selection processes in matrix–oligomer complexation reactions are far more important than expected. As a result, it is principally not possible to evaluate these reactions correctly in terms of a homodisperse model when heterodisperse samples are employed. With respect to the system under consideration, even the complexation behavior of oligomers with a dispersity number of 1.1 is not predicted correctly by the homodisperse model.

As a result of these selection processes, it is not possible to correlate directly the mixing ratio, at which a maximum heat of interaction is found, to the stoichiometric ratio of complexation, in the case of calorimetric investigations of matrix–oligomer systems. No problems of these kind will be met when only components of high molar mass are employed.

The selectivity of this kind of complexation reaction can be used to fractionate heterodisperse samples with respect to chain length as shown above for the case of the it-PMMA–st-PMMA system. In principle, to obtain the highest degree of selectivity, one has to use an excess of oligomers with regard to the matrix as shown above. However, in this system, showing second-order cooperativity, the associates formed tend to immobilize the system, preventing the exchange processes from occurring. As this second-order cooperativity is not unique to this system,[22] it might sometimes be better in practice to employ an excess of matrices to prevent this immobilization. In that case highest selectivity is met at the critical conditions as defined by eq 24. Finally, it should be mentioned that in this system, it is also possible to fractionate with respect to tacticity as shown by Schomaker et al.[8]

Acknowledgment. The assistance of E. J. Vorenkamp on writing the software for the simulations is gratefully acknowledged.

Registry No. 1 isotactic PMMA:2 syndiotactic PMMA complex, 79616-50-5.

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On the Chain Length Dependence of the Dynamics of Coil Expansion of Poly(methacrylic acid)

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ABSTRACT: The rate of chain expansion of poly(methacrylic acid) (PMA) in methanol solutions containing 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide (I) was measured by following the change in the light scattering intensity (LSI). Chain expansion was induced by the photolysis of I by a 20-ns flash of 265-nm light. OH^- ions generated in this way led to an increase in the degree of ionization of the PMA. The half-life of the LSI decrease reflecting the chain expansion depended on the molecular weight as $\tau_{1/2} \propto M^x$, with $x = 0.9$. On the basis of the Rouse–Zimm theory, $x = 1.5$ was expected. The discrepancy is explained in terms of the neutralization of PMA being a stepwise noncooperative process. Initially, the hydroxyl ions react almost exclusively with carboxylic groups in the outer regions of the rather compact PMA coils. Subsequently, the ionized sites equilibrate and thus become statistically distributed along the chains.

Introduction

The dynamics of conformation changes of polyelectrolytes can be measured conveniently with the aid of a technique based on a UV light induced pH jump accomplished by laser flash photolysis of an OH^- emitter such as the substituted triphenylmethane leucohydroxide I. This was recently demonstrated by Irie and Schnabel,[1] who investigated the chain expansion of poly(methacrylic acid) (PMA). Prior to that it was shown by Irie[2] that upon continuous irradiation of triphenylmethane leuco-

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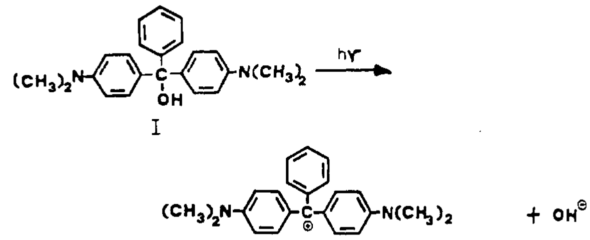

(1)

I, 4,4′-bis(dimethylamino)triphenylmethane leucohydroxide

hydroxides in aqueous solution, the pH increased very rapidly by several orders of magnitude after the light was switched on. The pH decreased again with a half-life of several minutes when the light was turned off.

In connection with our work, it is interesting to note that, also quite recently, Morawetz et al.[3] have studied chain expansion and contraction of poly(methacrylic acid) possessing dansyl side groups in aqueous solution by employing a stopped-flow pH-jump technique. When the dansyl groups are transferred from water to a less polar medium, the fluorescence intensity increases sharply; i.e., upon chain expansion after a sudden change in the degree of ionization, the dansyl groups can interact quite freely with water molecules with the consequence of a decrease in the emission intensity. Upon studying the expansion of the chain, these authors[3] detected several modes of decrease in the fluorescence intensity after mixing. The initial fast process occurring in the submillisecond time range and corresponding to about 40% of the change in the intensity of the emission of the dansyl groups was too rapid to be followed by the stopped-flow technique. The subsequent approach to equilibrium fitted biphasic kinetics.

The present paper describes results obtained in studies of the chain expansion of PMA in methanol. It is aimed at obtaining information on the chain length dependence of the dynamics of chain expansion by using polyelectrolyte samples possessing a narrow molecular weight distribution. By applying the laser flash method in conjunction with the light scattering detection method, we could resolve processes in the submillisecond time range. Methanol was used as solvent because both the leucohydroxide and PMA dissolved readily in it. It turned out that PMA expands in methanol in a manner similar to that in water and that chain expansion is a noncooperative process.

Experimental Section

(a) Materials. Methacrylic acid (E. Merck, for synthesis) was polymerized by irradiation of methanolic solutions containing 40% monomer with ^{60}Co γ-rays at room temperature at various intensities. The polymer samples were precipitated with ethyl acetate and reprecipitated with ethyl acetate from methanol solution. Fractionation of the polymer samples was performed with methanol solutions containing 1% polymer. Ethyl acetate was added to the polymer solutions in amounts sufficient to produce turbidity by precipitation of part of the polymer. The precipitated polymer was redissolved by cooling to 5 °C. Subsequently, the solution was heated to a temperature (higher than 15 °C) appropriate to precipitate a fraction of the polymer. GPC measurements in 0.2 M aqueous $NaClO_4$ solution yielded unimodal chromatograms. The molecular weight distribution was estimated to correspond to $M_w/M_n < 2$. The polymers used in this work are listed in Table I. Methanol (E. Merck, Uvasol) and LiCl (E. Merck, Suprapur) were used without further purification.

(b) Viscosity Measurements. The viscosity of methanol solutions of PMA samples was measured with capillary viscometers using a Schott apparatus (Model CT 150).

(c) Flash Photolysis Experiments. The polymer solutions were irradiated with 20-ns flashes of 265-nm light produced by a neodymium/YAG laser (J. K. Laser Ltd.) operated in conjunction with two frequency doublers. The absorbed dose per flash was about 4.5 J/L. For the light scattering measurements[4] an Ar ion laser (Spectra Physics, Model 165) was used as the source of the analytical light. Electrical conductivity measurements were performed by using a quartz cell equipped with a pair of platinum electrodes that were connected to an ac source (10 MHz).[5] Prior to irradiation the sample solutions were passed 4 times through filters of pore size 0.45 μm (Millipore).

Table I
Molecular Weights of the Poly(methacrylic acid) Samples

sample	$10^{-5}M_w$[a]	sample	$10^{-5}M_w$[a]
PMA-1	5.7	PMA-4	1.9
PMA-2	3.3	PMA-5	0.68
PMA-3	2.3	PMA-6	0.45

[a] Determined by light scattering in methanol solution with $dn/dc = 0.183$ mL/g.

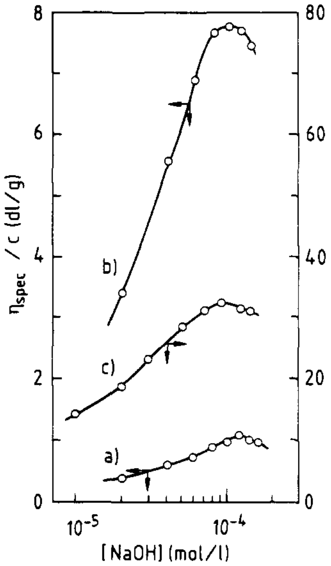

Figure 1. Chain expansion of PMA in methanol solution. The curves show the dependence of the reduced specific viscosity η_{sp}/c on the concentration of NaOH: curve a, PMA-6, $c_{PMA} = 0.1$ g/L; curve b, PMA-4, $c_{PMA} = 0.1$ g/L; curve c, PMA-1, $c_{PMA} = 0.1$ g/L.

Results and Discussion

(a) Chain Expansion by Neutralization with NaOH. PMA is a weak acid that ionizes upon neutralization with sodium hydroxide, yielding carboxylate anions according to reaction 2. In order to confirm that, upon ionization,

$$\wr\!-\mathrm{COOH} + \mathrm{NaOH} \longrightarrow \wr\!-\mathrm{COO^-Na^+} + \mathrm{H_2O} \qquad (2)$$

the polymer chains expand in methanol as they do in water, the reduced specific viscosity, η_{sp}/c, of PMA in methanol was measured as a function of NaOH concentration. As shown in Figure 1 for three PMA samples of different molecular weight, η_{sp}/c increased significantly when the NaOH concentration was increased from 10^{-5} to 10^{-4} mol/L. At a NaOH concentration of about 10^{-4} mol/L, corresponding to a degree of ionization of about 0.1, η_{sp}/c passed through a maximum. A pronounced salt effect was observed when small amounts of a low molecular weight salt, LiCl, were added to PMA solutions in methanol. At constant concentrations of PMA and NaOH, η_{sp}/c decreased with increasing LiCl concentration. As shown in Figure 2 for the case of PMA-1, the reduced specific viscosity decreased by a factor of about 3 when [LiCl] increased up to 10^{-3} mol/L.

The observed behavior is in accordance with the generally accepted concept of polyelectrolyte chains expanding

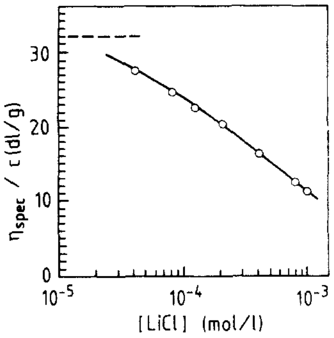

Figure 2. Salt effect on the viscosity of solutions of PMA-1. The solid line depicts the dependence of the reduced specific viscosity on the concentration of LiCl in methanol solution. $c_{PMA} = 0.1$ g/L; $c_{NaOH} = 7 \times 10^{-5}$ mol/L. The dotted line indicates the value of η_{sp}/c in the absence of LiCl.

due to intramolecular electrostatic repulsion between ionized pendant groups.[6-8] The increase of η_{sp}/c with increasing degree of ionization reflects chain expansion, and the decrease of η_{sp}/c upon addition of LiCl results from the electrostatic repulsion forces between carboxylate ions being weakened by the ions of the added salt with the consequence of chain contraction.[9] A similar screening effect also occurs upon neutralization, which leads to an increase in the total ionic strength of the solution. It is interesting to note that the latter screening effect becomes effective in methanol solutions at lower ionic strength when compared to aqueous solutions. This is due to the less polar nature of methanol. In conclusion, the results of the viscosity measurements indicate unambiguously the occurrence of chain expansion of PMA in methanol solution upon neutralization as a consequence of intramolecular electrostatic repulsion.

(b) Conformational Changes Induced by Laser Flash Photolysis. As has been shown earlier,[1] continuous irradiation of methanolic solutions of PMA containing the triphenylmethane leucohydroxide I led to a significant increase in the solution viscosity. This was explained in terms of chain expansion due to partial neutralization of PMA by hydroxyl ions generated according to reaction 1:

$$\sim COOH + OH^- \longrightarrow \sim COO^- + H_2O \qquad (3)$$

Reaction 3 with subsequent chain expansion was also achieved by irradiation of PMA in methanol containing I with a 20-ns flash of 265-nm light.[1] The ionic dissociation according to reaction 1 occurred very fast, i.e., during the flash, as was concluded from the fact that the optical absorption of the triphenylmethane cations around 600 nm was formed during the flash. Simultaneously, the electrical conductivity increased due to the generation of ions.

In the present work, irradiation of a solution containing 2×10^{-5} mol/L of I with a single flash led to an increase in the hydroxyl ion concentration of about 1×10^{-5} mol/L. Changes in the light scattering intensity (LSI) and in the electrical conductivity due to this change in [OH$^-$] were measured. Typical results are depicted in Figure 3, where oscillograms illustrating the change in LSI (Figure 3a) and in the electrical conductivity (Figure 3b) are shown. It can be seen that the electrical conductivity increased during the flash and that it decreased after the flash. Whereas the fast increase during the flash reflects the formation of carbocations and hydroxyl ions, the partial decrease is ascribed to the conversion of hydroxyl ions into the less mobile carboxylate ions attached to the polymer chains. The lifetime of the latter process was determined in this work to be somewhat less than 5 μs.

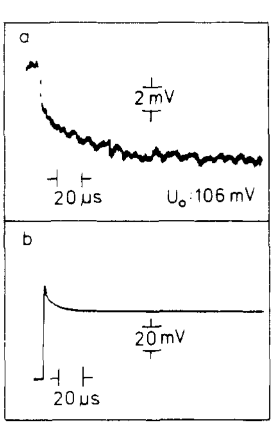

Figure 3. Flash photolysis of PMA-1 in methanol solution containing I (2×10^{-5} mol/L) and NaOH (2×10^{-5} mol/L). $c_{PMA} = 0.1$ g/L. Oscillograms depicting changes in (a) the LSI at 514 nm and (b) the electrical conductivity (ac, 30 V) during and after the flash (20 ns, $\lambda_{inc} = 265$ nm).

The LSI decreased according to two modes corresponding to a very rapid process and a slow process. The rapid mode, which corresponds to the initial unresolved portion of the trace in Figure 3a, reflects the increase in the optical absorption at 514 nm (the wavelength of the analytical light used for the LSI measurements) due to triphenylmethyl cations and probably in the refractive index increment due to the ionic dissociation of I. This rapid LSI change occurs during the flash and it is not associated with a conformational change. The slow mode of the LSI decrease, however, reflects an increase in the radius of gyration of the polymer coils according to the Debye equation:

$$\frac{Kc}{R_\vartheta} = \frac{1}{M_w} + \frac{16\pi^2\langle s^2\rangle}{3\lambda_0^2 M_w}\sin^2(\vartheta/2) + 2A_2c \qquad (4)$$

The light scattering intensity R_ϑ (Rayleigh ratio) is correlated to the weight-average molecular weight M_w, the mean square radius of gyration $\langle s^2\rangle$, and the second virial coefficient A_2. $K = (2\pi^2 n_0^2/N_A\lambda_0^4)(dn/dc)^2$. c is the polymer concentration, n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of the incident light, and N_A is Avogadro's number. Expansion of the polymer chains leads to an increase in $\langle s^2\rangle$, causing a decrease in the LSI.

The half-life of the relaxation process reflected by the slow mode of LSI decrease is of the same order of magnitude as that of the electrical conductivity decrease due to the neutralization process. However, a comparison of the traces in parts a and b of Figure 3 shows clearly that the neutralization process is faster. In the case treated in Figure 3 the half-life of the LSI change is 26 μs as compared to $\tau_{1/2} < 5$ μs obtained for the change in the electrical conductivity.

The assignment of the slow mode of LSI decrease to a conformational change in the PMA chains was confirmed by experiments with solutions of PMA-4 containing LiCl (8.4×10^{-4} mol/L) and NaOH (2×10^{-5} mol/L). As can be seen from Figure 2, this LiCl concentration was high enough to strongly prevent coil expansion. As shown in Figure 4b, only the fast mode of LSI change was detected in the presence of LiCl. The slow mode was completely suppressed. A similar result was obtained when the initial NaOH concentration was rather high. At [NaOH] = 1.4×10^{-4} mol/L, the slow mode was totally suppressed, as shown in Figure 4c. It can be seen from Figure 1, curve c, that, at this NaOH concentration, a small increase in the OH$^-$ concentration does not lead to a significant change

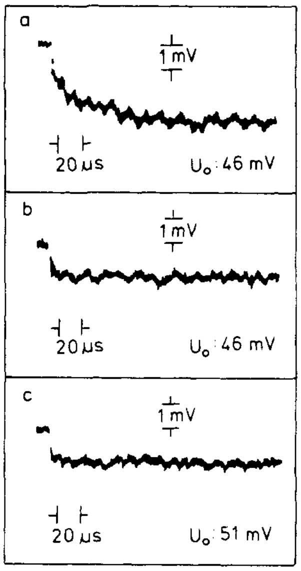

Figure 4. Flash photolysis of PMA-4 in methanol solution. Changes in the LSI in the presence of LiCl and at a higher NaOH concentration: (a) $c_{PMA} = 0.1$ g/L, $c_{NaOH} = 2 \times 10^{-5}$ mol/L; (b) $c_{PMA} = 0.1$ g/L, $c_{NaOH} = 2 \times 10^{-5}$ mol/L, $c_{LiCl} = 8.4 \times 10^{-4}$ mol/L; (c) $c_{PMA} = 0.1$ g/L, $c_{NaOH} = 1.4 \times 10^{-4}$ mol/L.

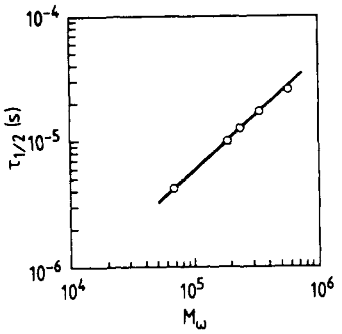

Figure 5. Dependence of the half-life of LSI decrease (slow mode) on the molecular weight. PMA in methanol solution (0.1 g/L) containing I (2×10^{-5} mol/L) and NaOH (2×10^{-5} mol/L). $D_{abs} = 1 \times 10^{-5}$ einstein/L.

in the conformation and should, therefore, have little or no effect on the LSI.

In conclusion, the results presented in Figure 4 corroborate the assignment of the slow mode of the LSI decrease, demonstrated in Figures 3a and 4a, to a change in the conformation.

(c) Dependence of the Rate of Coil Expansion on the Chain Length. Figure 5 shows the dependence of the half-life of the slow mode of the LSI change on the average molecular weight. These experiments were also carried out in methanol solution containing NaOH at a concentration corresponding to an initial degree of neutralization $\alpha_{n,0} = 0.017$. Irradiation of the PMA solutions with a 20-ns flash of 265-nm light (absorbed dose D_{abs} = ca. 1×10^{-5} einstein/L) resulted in an increase of α to $\alpha_{n,D} = 0.026$. The slope of the straight line in Figure 5 corresponds to the relationship $\tau_{1/2} \propto M_w^x$, with $x = 0.9$. It is interesting to note that according to the theory of Rouse[10] and Zimm,[11] which is based on the bead and spring model, a higher value of x would be expected, as is described below.

For the free-draining case the dependence of the relaxation time τ_k on the molecular weight can be derived from

$$\tau_k = \frac{6M\eta_s[\eta]}{\pi^2 RTk^2} \tag{5}$$

Here, τ_k is the relaxation time for the kth mode, M is the molecular weight, η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, and k is the number of normal modes. With $[\eta] \propto M^\nu$ one obtains

$$\tau_k \propto M^{1+\nu} \tag{6}$$

(Notably, the same proportionality is obtained for the non-free-draining case.) According to Wiederhorn and Brown,[12] $\nu = 0.5$ for PMA in methanol at 26 °C. Thus, $x = 1 + \nu = 1.5$ is expected, which is significantly higher than $x = 0.9$ found experimentally.

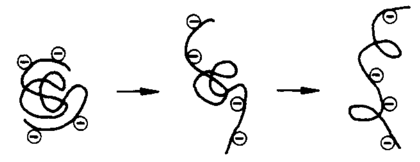

Figure 6. Schematic illustration of the two phases of chain expansion in the course of neutralization of PMA with hydroxyl ions.

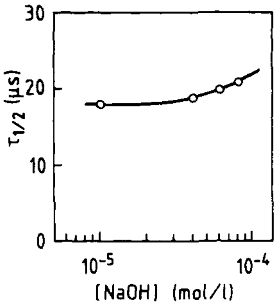

Figure 7. Dependence of the half-life of the LSI decrease on the concentration of NaOH. PMA-2 in methanol solution (0.1 g/L). I = 2×10^{-5} mol/L).

The applicability of eq 5 has been tested by other authors. Adachi and Kotaka,[13] for example, measured the dielectric loss factor for poly(2,6-dichloro-1,4-phenylene oxide) in dichlorobenzene and found that eq 5 holds for the dependence of the frequency of the maximum dielectric loss on the molecular weight. If it is assumed that eq 5 also holds for the present case, the discrepancy in the values of the exponent x must indicate the nonapplicability of one of the basic assumptions made for the derivation of eq 5. Actually, the relaxation time derived from the Rouse–Zimm theory reflects a motion involving the whole macromolecule. In our case, however, it is quite probable that the macromolecules cannot respond in total but only partially to a sudden change in the hydroxyl ion concentration. This can be envisaged in terms of rather compact polymer coils in which not all segments are accessible to the interacting hydroxyl ions. Consequently, the initial neutralization process should be restricted to the outer regions of the coils. In this initial phase only these outer regions can expand due to electrostatic repulsion, and the cores of the coils remain more or less unperturbed. At a later stage, an equilibration process in which the ionized sites are distributed along the chains becomes operative, with the result that chain expansion pertains to whole chains. This is schematically illustrated in Figure 6. Formally, this behavior can be treated on the basis of the following relationship between the relaxation time and the molecular weight:

$$\tau \propto M^{1+\nu-\gamma} \quad (0 < \gamma < 1) \tag{7}$$

γ can be taken as a measure for the compactness of the coils. For compact coils γ is close to unity. At constant M, γ decreases with increasing coil size. When the coil size was increased in the present case by increasing the initial degree of ionization, the half-life of the LSI decrease became longer. This is shown in Figure 7.

In conclusion, the results obtained in this work appear to indicate that chain expansion of PMA in methanol induced by a sudden increase in the degree of ionization does not occur as a cooperative process but instead as a stepwise process involving initially only the outer regions of the coils. This takes place in the microsecond time range. Subsequently, a statistical distribution of ionized sites is established in a rather slow equilibration process. The relaxation process observed by Morawetz et al.[3] in the time range of seconds probably corresponds to this equilibration process. Attempts to detect the slow process in the present work were not successful because the light scattering setup did not allow measurements of small LSI changes at long time scales.

Acknowledgment. The poly(methacrylic acid) samples were synthesized and characterized by R. Zuch, U. Fehrmann, and M. Weller at the Hahn-Meitner-Institut. The valuable assistance of Dr. G. Beck during the flash photolysis experiments is gratefully acknowledged.

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Fiber Spinning from the Nematic Melt. 3. The Copolyester of *p*-Hydroxybenzoic Acid and 2-Hydroxy-6-naphthoic Acid

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ABSTRACT: Rheological measurements and fiber spinning were performed for the copolyester of *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid furnished by Celanese Corp. This polymer softens at 222 °C and the DSC melting endotherm occurs at 247 °C. Fibers were spun from the melt at temperatures of 250, 260, and 280 °C, taking the spin draw ratio as a variable at each temperature. The initial modulus, breaking tenacity, and elongation to break were measured. The structure of the fibers was characterized by wide-angle X-ray diffraction and differential scanning calorimetry measurements. The initial modulus, M_0, for fibers spun at 260 or 280 °C increases strongly at low spin draw ratios and reaches a plateau value, about 425 g/denier, at a spin draw ratio of 135. This is over twice the value we obtained for the copolyester of poly(ethylene terephthalate) containing 60 mol % *p*-oxybenzoate units. The initial modulus of fibers spun at 250 °C increases more slowly with spin draw ratio and reaches a plateau value of only 220 g/denier at a spin draw ratio of 60. The breaking tenacity of fibers spun at 260 or 280 °C exhibits a sharp peak when plotted as a function of the spin draw ratio. When the melt was preheated to 280 °C before spinning at 250 °C, the fiber properties coincided with those of fibers spun at 260 or 280 °C without preheating. Heat treatment of the fibers increases the inherent viscosity, the degree of crystallinity, and the crystal melting temperature. However, heat treatment improves the fiber properties only if the spin draw ratio is high, but not for fibers collected at low spin draw ratios. These findings are discussed in terms of the crystallite orientation, degree of crystallinity, and rheological properties.

Introduction

Thermotropic liquid crystal polyesters have attracted considerable attention due to their ease of processing and good mechanical properties. One of the earliest of these to become available in quantity is the copolymer of poly(ethylene terephthalate) and *p*-hydroxybenzoic acid supplied by Tennessee Eastman Co.[1-3] The rheological[1-11] and fiber properties[1,2,11-15] of this polymer have been investigated by a number of workers. More recently, a series of thermotropic polyesters disclosed by Calundann[16,17] has become commercially available from Celanese Corp. One of these is a random copolymer of *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid, which we will designate as HBA/HNA. Blackwell and co-workers[18-20] studied the molecular structure of this polymer by X-ray diffraction. They reported good agreement between the observed *d* spacings of the meridional reflections and those calculated under the assumption that the sequence of monomers is random. Stamatoff[21] and Donald and Windle and co-workers[22-24] studied the effect of annealing upon the texture. There appears to be some rearrangement in packing but no development of three-dimensional order in this copolymer. Blundell[25] has estimated a crystallinity of about 20% for the copolymer containing 60 mol % HNA. On the other hand, Butzbach and co-workers,[26] from thermal studies, predicted a long-range three-dimensional order and a high degree of crystallinity. Only a few studies of the behavior in fiber spinning have been reported.[16,17,27,28]

Experimental Section

The random copolyester of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) containing 42 mol % HNA was kindly supplied by Celanese Corp. We will designate this

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