

in eq A.6 are reported<sup>3</sup> as being  $B = 1.0$  and  $v_{f,cr2} = 0.066$ .

The variations of  $k_p$  with  $w_p$  for MMA at 50 °C predicted by the above three models are compared with the experimentally observed variation<sup>1</sup> in Figure 4. It is seen that none of the above variants of free volume theory gives an adequate description of diffusion-controlled propagation. This is further illustrated by the fact that a value of  $k_p = 4.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is extrapolated for  $w_p = 1.0$  (pure polymer) from the experimental measurements<sup>1</sup> (see eq 1), whereas the Soh-Sundberg model (eq A.1 and A.2) gives  $k_p = 1.5 \times 10^{-23} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for this  $w_p$ , the Marten and Hamielec model (eq A.6)  $1.4 \times 10^{-26} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and the Stickler model (eq A.1 and A.5)  $6.7 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (the relatively good agreement in this case between the Stickler prediction and experiment is redressed by the inability of this model to predict the point of onset of diffusion control [see Figure 4]). This level of agreement is extremely poor, especially when it is considered that these models (with the exception of that of Soh and Sundberg) contain adjustable parameters.

While many variations of the three models for  $k_p$  exist, all of these appear to concentrate on the variation of the adjustable parameters with experimental conditions (e.g., temperature and initiator type). The equations that result are therefore comparable to, if not identical with, one of the above types. Another common practice<sup>3,5</sup> is to use the "universal" free volume expressions of Kelley and Bueche<sup>26</sup> in lieu of those used above (eq A.4). This practice could not be adopted for the present calculations because the Kelley-Bueche equations yield a negative value for  $\nu_{fp}$  for poly-MMA at 50 °C, which is physically impossible.

Registry No. MMA, 80-62-6; AVN, 4419-11-8; AIBN, 78-67-1; LPO, 105-74-8.

## References and Notes

- Ballard, M. J.; Gilbert, R. G.; Napper, D. H.; Pomery, P. J.; O'Sullivan, P. W.; O'Donnell, J. H. *Macromolecules* 1986, 19, 1303.

## Influence of the Tacticity of Poly(methyl methacrylate) on Its Miscibility with Chlorinated Polymers

Even Lemieux and Robert E. Prud'homme\*

Centre de recherche en sciences et ingénierie des macromolécules (CERSIM), Département de chimie, Université Laval, Québec (Québec), Canada G1K 7P4

Rosalia Forte, Robert Jérôme,\* and Philippe Teyssié

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman B-4000, Liège, Belgium. Received September 11, 1987

**ABSTRACT:** Differential scanning calorimetry was used to determine the miscibility behavior of poly(methyl methacrylate) (PMMA)/chlorinated polymer blends. Nine PMMA's differing in tacticity were blended with three chlorinated polymers: poly(vinyl chloride) (PVC), a chlorinated PVC having a chlorine content of 68% (CPVC), and Saran, which is a random copolymer of vinyl chloride (12%) and vinylidene chloride (88%). The results show that all these PMMA's are miscible with PVC, CPVC, and Saran under proper thermal treatments and especially at 298 K. They all exhibit a lower critical solution temperature (LCST) which varies as a function of the microstructure of PMMA and the chlorine content of the chlorinated polymer. This LCST increases with the syndiotactic content for PMMA's blended with PVC or CPVC but decreases with the syndiotactic content of PMMA for Saran/PMMA blends. An increase in the chlorine content of the chlorinated polymer results in a decrease of the temperature of phase separation except for highly isotactic PMMA where the temperature of phase separation increases with the chlorine content. When the sample is annealed between its LCST and its  $T_g$ , miscibility is obtained. When the sample is annealed above its LCST, phase separation occurs. Correlations are made between the phase behavior of these polymer blends and the specific interactions occurring between them.

## Introduction

A large number of aliphatic and aromatic polyesters are miscible with chlorinated polymers, including poly(vinyl

- See, for example: Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 127.
- Marten, F. L.; Hamielec, A. E. *Am. Chem. Soc., Symp. Ser.* 1979, 104, 43.
- Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* 1982, 20, 1331. Sundberg, D. C., private communication.
- Stickler, M. *Makromol. Chem.* 1982, 184, 2563.
- Lau, W.; Westmoreland, D. G.; Novak, R. W. *Macromolecules* 1987, 20, 457.
- Hidi, P., private communication.
- Wunderlich, W.; Stickler, M. *Polym. Sci. Technol.* 1985, 31, 505.
- Lee, J. A.; Frick, T. S.; Huang, W. J.; Lodge, T. P.; Tirrell, M. *Polym. Prepr.—Am. Chem. Soc., Div. Polym. Chem.* 1986, 28, 369.
- Brandrup, A.; Immergut, E. H. *Polymer Handbook*; Wiley-Interscience: New York, 1975.
- Smoluchowski, M. *Z. Phys. Chem.* 1918, 92, 129.
- Schulz, G. V. *Z. Phys. Chem. (Frankfurt am Main)* 1956, 8, 290.
- Russell, G. T.; Napper, D. H.; Gilbert, R. G. *Macromolecules*, preceding paper in this issue.
- Reid, R. C.; Sherwood, T. K. *Properties of Gases and Liquids; Their Estimation and Correlation*; McGraw-Hill: New York, 1958.
- Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley-Interscience: New York, 1970.
- Einstein, A. *Ann. Phys.* 1905, 17, 549.
- See, for example: Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* 1983, 36, 1573. Moad, G., private communication.
- Noyes, R. M. *J. Chem. Phys.* 1954, 22, 1349. Noyes, R. M. *J. Am. Chem. Soc.* 1955, 77, 2042.
- Stickler, M.; Panke, D.; Hamielec, A. E. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 2243.
- Balke, S. T.; Hamielec, A. E. *J. Appl. Polym. Sci.* 1973, 17, 905.
- Panke, D.; Stickler, M.; Wunderlich, W. *Makromol. Chem.* 1983, 184, 175.
- Ballard, M. J.; Napper, D. H.; Gilbert, R. G. *J. Polym. Sci., Polym. Chem. Ed.* 1984, 22, 3225.
- See, for example: Eisenberg, A. In *Physical Properties of Polymers*, American Chemical Society: Washington, D.C., 1984.
- Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* 1976, 9, 302.
- DeSchringer, F.; Smite, G. *J. Polym. Sci. A-1* 1966, 4, 2201.
- Kelley, F. N.; Bueche, F. *J. Polym. Sci.* 1961, 50, 549.

chloride) (PVC), chlorinated PVC (CPVC), and Saran (a statistical copolymer containing at least 80% of vinylidene chloride co-units).<sup>1-8</sup> The miscibility of these blends is due

to the presence of specific interactions between the carbonyl groups of the polyester and the chlorinated polymer, the exact nature of these interactions being still under investigation.<sup>4-7,9-11</sup>

Several polymethacrylates have also been reported to give miscible blends with chlorinated polymers. Walsh et al.<sup>12,13</sup> have observed that chlorinated polyethylene/poly(methyl methacrylate) (CPE/PMMA) blends are miscible if the chlorine content of the former is larger than 49%. Furthermore, Walsh and McKeown<sup>14</sup> have found that PVC is miscible with poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-propyl methacrylate), poly(*n*-butyl methacrylate), poly(*n*-amyl methacrylate), and poly(*n*-hexyl methacrylate), despite an earlier report claiming the immiscibility of PVC/PMMA blends.<sup>15</sup> With use of differential scanning calorimetry, Tremblay and Prud'homme<sup>16</sup> have demonstrated that a high chlorine content for the chlorinated polymer and an optimum  $\text{CH}_2/\text{COO}$  ratio for the polymethacrylate are necessary requirements to obtain miscibility. The latter condition defines the presence of a "miscibility window" in those systems. At high and low COO concentrations, immiscibility is observed. At intermediate COO concentrations, inside the "miscibility window", miscibility is found. Walsh and Cheng<sup>17</sup> reached the same conclusion by measuring heats of mixing of oligomeric analogues of various polyacrylates and polymethacrylates with PVC. Their results were interpreted by considering the dispersive forces and specific interactions contributions to the heat of mixing, this latter contribution overcoming the unfavorable contribution of the former.

The tacticity of PMMA also seems to have a great influence on its miscibility with chlorinated polymers. Schurer et al.<sup>18</sup> have shown that isotactic PMMA and PVC form an inhomogeneous system over the entire composition range whereas blends of syndiotactic PMMA and PVC give an homogeneous mixture up to a composition corresponding to a ratio of repeat units of about 1:1. In contrast, using the method of thermally stimulated depolarization currents, Vanderschueren et al.<sup>19</sup> have reported a certain degree of miscibility of blends of syndiotactic PMMA with PVC only at PMMA concentrations smaller than 10%. Using pulsed NMR and nonradiative energy-transfer measurements, Albert et al.<sup>20</sup> have observed heterogeneities in PVC/syndiotactic PMMA blends and emphasized the importance of factors such as the method of mixing, tacticity, molecular weight, and polydispersity upon the homogenization of the system. Finally, Woo et al.<sup>21</sup> found that Saran is miscible with atactic and isotactic PMMA.

The occurrence of a phase separation between PMMA and various chlorinated polymers upon an increase in temperature has been reported by Walsh et al.<sup>12,22</sup> These authors observed in many systems a lower critical solution temperature (LCST) that increases with the chlorine content of the chlorinated polymer. Also, Jager et al.<sup>23</sup> have reported that atactic PMMA blended with PVC is miscible at all compositions when treated at 333 K. Melt blending at 453 K leads to phase separation. The equilibrium LCST of this blend was also shown to increase with the decrease of the molecular weight of one or both polymers in the mixture.

The occurrence of a LCST seems to be also related to the tacticity of PMMA. In a recent study, Vorenkamp et al.<sup>24</sup> have shown that not only atactic PMMA but also a syndiotactic PMMA and three isotactic PMMA's, having similar tacticities but different molecular weights, show a LCST behavior and can be made miscible with PVC if a proper molecular weight is chosen, provided that blends

Table I  
Characterization of the Polymers

polymer	acronym	tacticity (i:h:s)	$M_w$ , kg/mol	$M_w/M_n$	$T_g$ , K
poly(methyl methacrylate) isotactic	ISO-1	100:0:0	294	7.4	327
	ISO-2	85:15:0	45	5.6	320
	ISO-3	63:24:13	291	3.0	329
	ISO-4	46:33:21	120	3.0	332
atactic	ATA-1	15:39:46	84	1.8	356
	SYN-1	5:26:69	92	1.4	372
syndiotactic	SYN-2	4:21:75	111	1.7	377
	SYN-3	0:18:82	117	1.1	399
	SYN-4	3:14:83	84	1.2	405
chlorinated polymer poly(vinyl chloride)	PVC		80		345
chlorinated PVC	CPVC-68		215	2.3	388
Saran <sup>a</sup>			100	2.3	280

<sup>a</sup> Random copolymer of vinyl chloride (12%) and vinylidene chloride (88%)

are prepared or annealed below the temperature of phase separation. Differences in phase behavior of these different systems were ascribed to differences in free volumes between the various PMMA's, which is also function of molecular weight.

This latter study then suggests a regular variation of LCST with the tacticity of PMMA. It also suggests, indirectly, that other chlorinated polymers can be miscible with those PMMA's if they are prepared under proper conditions. It is then the purpose of this paper to study the miscibility behavior of several chlorinated polymer/poly(methyl methacrylate) blends. More specifically, blends have been prepared from nine PMMA's greatly differing in tacticity and from PVC, chlorinated PVC, and Saran. Their miscibility and phase separation behavior have been estimated from their glass transition temperature as a function of composition, using differential scanning calorimetry.

## Experimental Section

Table I lists the poly(methyl methacrylates) and the chlorinated polymers used in this study. Two isotactic PMMA samples were obtained from Polymer Laboratories (ISO-1 and ISO-2) while the atactic sample (ATA-1) was supplied by Fisher Scientific. Every other stereoregular PMMA sample was prepared by anionic polymerization under anhydrous conditions in a toluene/tetrahydrofuran cosolvent mixture by using ( $\alpha$ -methylstyryl)lithium as initiator. A careful control of the temperature and cosolvent ratio enables one to prepare PMMA samples with a specific tactic content.<sup>25</sup> Poly(vinyl chloride) (PVC) was obtained from Shawinigan Chemicals while the chlorinated PVC, containing 68 wt % chlorine, was supplied by Chloé Chimie. The Saran, which is a random copolymer of vinyl chloride and vinylidene chloride, contained 88% of the latter repeat unit and was purchased from Polysciences Chemical Co.

The tacticity of the PMMA samples was determined by nuclear magnetic resonance from 10% *o*-dichlorobenzene solutions, at 408 K, with a Varian XL-200 instrument.<sup>26</sup> Molecular weights were determined by size exclusion chromatography (SEC) using  $\mu$ -styragel columns and a Waters chromatograph. The measurements were conducted at 298 K in tetrahydrofuran, and the apparatus was calibrated with polystyrene standards.

Blends were prepared by slowly casting films from solution by using distilled tetrahydrofuran. In all cases, solvent evaporation was conducted at room temperature. The resulting films were removed from petri dishes and dried in a vacuum oven at room temperature until they reached constant weight.

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer. The DSC was calibrated with ultrapure indium. The glass transition temperatures,  $T_g$ , reported in this

paper were recorded at the half-height of the corresponding heat capacity jump.

After their insertion in the DSC apparatus, all samples were first cooled to 268 K and maintained at that temperature for 5 min. A first scan was made at a heating rate of 40 K/min, up to 423 K. Each sample was maintained 3 min at that temperature in order to remove the last traces of solvent and quenched to 268 K. It was again left 5 min at this temperature before a second scan was performed at a heating rate of 20 K/min. The  $T_g$ 's reported in this paper were always recorded during the second scan. A third scan was run on some selected samples to check the reproducibility of the measured values.

In this paper, the following terminology is retained: a sample is considered miscible if it gives at each composition a single  $T_g$  intermediate between those of the individual components. Thus, a sample exhibiting two  $T_g$ 's at a given composition is considered immiscible, even if the possibility of observing a single  $T_g$  at other compositions is not excluded.

The phase separation occurring between PMMA's and chlorinated polymers was studied with the following annealing cycle. The samples were first cooled to 268 K and maintained at that temperature for 5 min. A first scan was made at a heating rate of 40 K/min, up to an annealing temperature superior by 10 K to the highest  $T_g$  of the homopolymers considered. Each sample was maintained 3 min at that temperature and quenched to 268 K. It was again left 5 min at this temperature before a second scan was performed at a heating rate of 40 K/min, the annealing temperature for this additional scan being 10 K higher than the annealing temperature of the previous scan. Such a heating-cooling cycle was repeated until two well-defined  $T_g$ 's could be observed. The annealing temperature at which two  $T_g$ 's begin to be observed corresponds approximately to the temperature where phase separation occurs.

## Results

Table II gives  $T_g$  values of PVC/PMMA blends prepared at an annealing temperature of 423 K. According to the single  $T_g$  criterion, PVC blends with ISO-3, ISO-4, ATA-1, SYN-1, SYN-2, SYN-3, and SYN-4 are found miscible while the others are immiscible.

However, we note for PVC/ISO-3, PVC/ISO-4, and PVC/ATA-1 blends that the  $T_g$ 's of the respective homopolymers are separated by less than 20 K. A careful examination of the DSC curves do not show any indication of the presence of a second  $T_g$  at the temperatures where the  $T_g$ 's of the two homopolymers are expected. In contrast, the PVC/ISO-1 blends exhibit two  $T_g$ 's as a function of composition. These latter blends are, therefore, considered immiscible with the formation of two phases composed almost entirely of pure PMMA and pure PVC.

The PVC/ISO-2 blends also exhibit two  $T_g$ 's, one which is close to that of the PVC homopolymer and another which is composition-dependent. This sort of result indicates that these immiscible blends are in fact composed of a pure PVC homopolymer phase and of a PMMA-rich phase, in which some PVC is dissolved.

Table III gives  $T_g$  values of CPVC/PMMA blends prepared at an annealing temperature of 423 K. Every CPVC/syndiotactic PMMA blend is found miscible while the CPVC/ISO-2, CPVC/ISO-3, CPVC/ISO-4, and CPVC/ATA-1 blends are immiscible in agreement with previously published results.<sup>16,27</sup> These latter mixtures do not necessarily exhibit two  $T_g$ 's at every composition. For instance, CPVC/isotactic PMMA blends show two  $T_g$ 's at CPVC contents of 50 and 75% but only one  $T_g$  at a CPVC content of 25%.

Table IV gives  $T_g$  values of Saran/PMMA blends prepared at an annealing temperature of 423 K. The Saran/ISO-2, Saran/ISO-3, Saran/ISO-4, and Saran/ATA-1 blends exhibit a single  $T_g$  intermediate between those of the respective homopolymers and are, therefore, miscible. These results are then in agreement with the published

Table II  
DSC Analysis of PVC/PMMA Blends

PMMA	PVC in blend, wt %	$T_g$ , K	transition width, deg
ISO-1	100	345	23
ISO-1	75	349, 327	16, 21
ISO-1	40	355, 334	20, 27
ISO-1	25	348, 329	18, 18
ISO-1	0	327	25
ISO-2	100	345	23
ISO-2	75	348, 335	21, 16
ISO-2	50	348, 330	18, 13
ISO-2	25	342, 325	15, 22
ISO-2	0	320	19
ISO-3	100	345	23
ISO-3	75	343	24
ISO-3	50	341	37
ISO-3	25	333	30
ISO-3	0	329	26
ISO-4	100	345	23
ISO-4	75	341	31
ISO-4	50	344	37
ISO-4	25	342	37
ISO-4	0	332	27
ATA-1	100	345	23
ATA-1	75	353	28
ATA-1	50	350	40
ATA-1	25	354	36
ATA-1	0	356	19
SYN-1	100	345	23
SYN-1	74	358	22
SYN-1	50	361	19
SYN-1	25	382	44
SYN-1	0	372	19
SYN-2	100	345	23
SYN-2	75	370	24
SYN-2	49	367	19
SYN-2	25	383	36
SYN-2	0	377	17
SYN-3	100	345	23
SYN-3	75	361	20
SYN-3	50	363	45
SYN-3	25	391	37
SYN-3	0	399	19
SYN-4	100	345	23
SYN-4	75	363	24
SYN-4	50	373	24
SYN-4	25	395	14
SYN-4	0	405	18

data of Woo et al.<sup>21</sup> In contrast, Saran/SYN-1 blends show two  $T_g$ 's at Saran contents of 49 and 25% but only one at a Saran content of 75%. In this latter case, the broadness of the transition width is such that dispersion at the molecular level is not ascertained. We must keep in mind that the scale of the  $T_g$  measurement is of the order of 15 nm<sup>28</sup> and that the observation of a single  $T_g$  does not necessarily imply that the two polymers are dispersed at the molecular level. Every other Saran/syndiotactic PMMA blends clearly show two  $T_g$ 's at every composition studied and are thus considered immiscible.

The phase behavior reported above refers to samples that were annealed at 423 K before analysis. As has been mentioned in the Introduction, blends with PMMA often exhibit a LCST<sup>12,22-24</sup> and different thermal treatments should lead to different observations. This possibility was checked by DSC with selected samples.

Figure 1 gives the thermograms of a PVC/ISO-2 blend having an ISO-2 content of 75%, a mixture which was reported immiscible in Table II. The thermograms obtained after annealing at 353, 363, and 373 K show a single  $T_g$  which is relatively broad. However, two distinguishable

Table III  
DSC Analysis of CPVC/PMMA Blends

PMMA	CPVC in blend, wt %	$T_g$ , K	transition width, deg
ISO-2	100	388	27
ISO-2	75	382, 335	40, 31
ISO-2	50	385, 327	23, 15
ISO-2	25	323	15
ISO-2	0	320	19
ISO-3	100	388	27
ISO-3	75	381, 334	30, 26
ISO-3	50	378, 341	19, 35
ISO-3	25	331	48
ISO-3	0	329	26
ISO-4	100	388	27
ISO-4	75	381, 331	30, 24
ISO-4	50	375, 334	14, 26
ISO-4	25	337	41
ISO-4	0	332	27
ATA-1	100	388	27
ATA-1	75	382	28
ATA-1	50	385, 361	7, 24
ATA-1	25	368	27
ATA-1	0	356	19
SYN-1	100	388	27
SYN-1	75	384	39
SYN-1	50	385	30
SYN-1	25	388	32
SYN-1	0	372	19
SYN-2	100	388	27
SYN-2	75	377	33
SYN-2	50	382	23
SYN-2	25	380	25
SYN-2	0	377	17
SYN-3	100	388	27
SYN-3	75	387	30
SYN-3	50	384	26
SYN-3	25	385	29
SYN-3	0	399	19
SYN-4	100	388	27
SYN-4	75	402	17
SYN-4	50	404	17
SYN-4	25	401	20
SYN-4	0	405	18

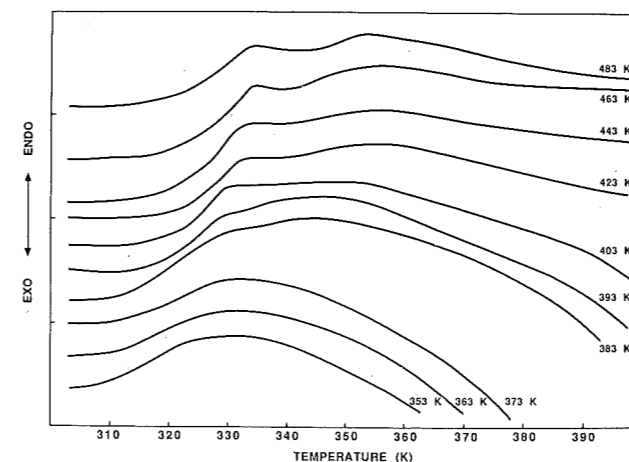


Figure 1. DSC thermograms of PVC/ISO-2 (25/75) blends which were annealed 3 min at the indicated temperature before quenching and scanning.

$T_g$ 's appear between 383 and 483 K. Therefore, a thermally induced phase separation occurs for this blend at a temperature between 373 and 383 K.

Similar experiments were conducted with other blends and other compositions. Figure 2 illustrates the phase behavior of PVC/ISO-2 and PVC/SYN-4 blends as a function of composition. For PVC/ISO-2 blends, a tem-

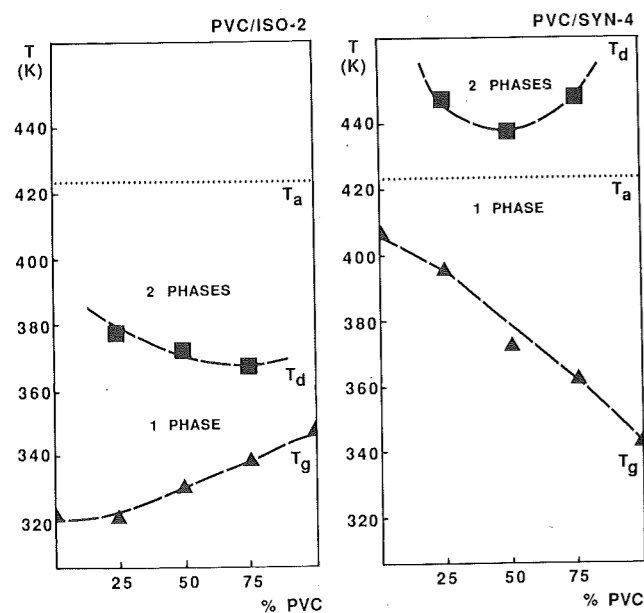
Table IV  
DSC Analysis of Saran/PMMA Blends

PMMA	Saran in blend, wt %	$T_g$ , K	transition width, deg
ISO-2	100	280	16
ISO-2	75	292	18
ISO-2	50	300	25
ISO-2	25	305	25
ISO-2	0	320	19
ISO-3	100	280	16
ISO-3	75	284	22
ISO-3	50	295	24
ISO-3	25	328	22
ISO-3	0	329	26
ISO-4	100	280	16
ISO-4	75	292	34
ISO-4	50	300	20
ISO-4	25	342	26
ISO-4	0	332	27
ATA-1	100	280	16
ATA-1	75	296	20
ATA-1	50	317	36
ATA-1	25	326	25
ATA-1	0	356	19
SYN-1	100	280	16
SYN-1	75	283	34
SYN-1	49	285, 375	32, 15
SYN-1	25	282, 377	24, 16
SYN-1	0	372	19
SYN-2	100	280	16
SYN-2	75	308, 393	39, 20
SYN-2	50	316, 387	38, 18
SYN-2	25	321, 382	40, 14
SYN-2	0	377	17
SYN-3	100	280	16
SYN-3	75	319, 375	48, 25
SYN-3	50	321, 386	44, 31
SYN-3	25	314, 396	39, 42
SYN-3	0	399	19
SYN-4	100	280	16
SYN-4	75	287, 396	28, 11
SYN-4	50	284, 379	29, 17
SYN-4	25	288, 376	21, 10
SYN-4	0	405	18

perature of phase separation ( $T_d$ ) is observed at each composition in the 368–378 K range. Furthermore, this phase separation occurs at sufficiently low temperatures to permit the observation of two distinguishable  $T_g$ 's at all compositions for an annealing temperature ( $T_a$ ) of 423 K, thus confirming the immiscibility behavior reported in Table II. However, when these blends are annealed at a temperature that is lower than the temperature of phase separation, one obtains a single composition-dependent  $T_g$  intermediate between those of the corresponding homopolymers.

Figure 2 illustrates a similar phase behavior with PVC/SYN-4 blends. In this case, the temperature of phase separation is in the 438–448 K range. This temperature of phase separation appears well above the annealing temperature of 423 K used before, and, therefore, a single  $T_g$  was observed at all compositions for an annealing temperature of 423 K.

These two series of measurements suggest that the presence of a LCST may be a general phenomenon in these systems and that miscibility may be found in all cases if an appropriate thermal treatment is used. In order to verify this assumption, we carried out similar measurements using ISO-2, ISO-3, ISO-4, ATA-1, and SYN-4 PMMA's blended with PVC, CPVC, and Saran and their phase behavior was estimated at three different compositions. The temperatures of phase separation recorded



**Figure 2.** Phase behavior of PVC/ISO-2 and PVC/SYN-4 blends as a function of composition.  $T_g$  is the glass transition temperature,  $T_d$ , the temperature of phase separation, and  $T_a$ , the annealing temperature.

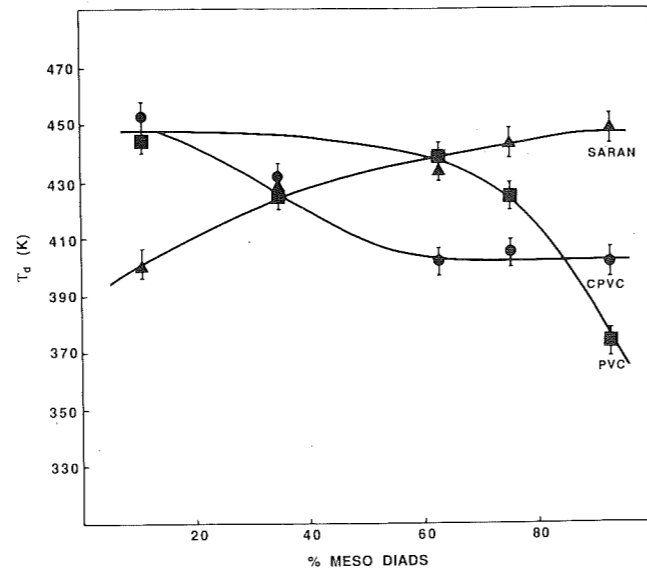
**Table V**  
Demixing Temperatures ( $T_d$ ) Recorded for Chlorinated Polymer/PMMA Blends

PMMA	% PMMA	$T_d$ , K		
		PVC	CPVC	Saran
ISO-2	25	368	388	458
	50	373	398	438
	75	378	418	448
ISO-3	25	438	408	468
	50	418	398	428
	75	418	408	433
ISO-4	25	438	388	428
	50	428	388	438
	75	448	428	438
ATA-1	25	428	438	438
	50	418	418	428
	75	428	428	428
SYN-4	25	448	468	418
	50	438	448	398
	75	448	448	388

for these systems are given in Table V. From this table, one can see that, indeed, a temperature of phase separation is detected in each system. In addition, it is not, for a given polymer blend, strongly dependent upon its composition. Average temperatures instead of the individual  $T_d$ 's can then be used, for each blend, in order to simplify the discussion.

Therefore, Figure 3 gives the average  $T_d$ 's obtained for these blends against the meso diad content in PMMA. PVC/PMMA and CPVC/PMMA blends behave in a similar manner: an increase in the meso diad content of PMMA leads to a decrease of the average  $T_d$ . This is in agreement with previously published data reporting a decrease of the LCST of PVC/PMMA blends when going from a syndiotactic, to an atactic, to an isotactic PMMA.<sup>23,24</sup> Figure 3 also shows that an increase in the chlorine content of the chlorinated polymer blended with PMMA results in a decrease of the average  $T_d$ . There is an exception to this general trend: the average  $T_d$  of the blend involving the highly isotactic PMMA increases with the chlorine content.

As for Saran/PMMA blends, an increase in the meso diad content of PMMA results in an increase of their



**Figure 3.** Variation of the phase separation temperature ( $T_d$ ) of chlorinated polymer/PMMA blends as a function of the PMMA meso diad content.

average temperatures of phase separation. This increase is quite considerable if we compare Saran/SYN-4 with Saran/ISO-4 blends. Furthermore, this tendency is just the reverse of that noticed with PVC and CPVC,  $T_d$  increasing with the meso diad content in the former case and decreasing in the two latter cases.

#### Discussion and Conclusions

The above results clearly show that all PMMA's, whatever their tacticity, can be rendered miscible with PVC, CPVC, and Saran under proper thermal treatments. Miscibility is maintained as long as these blends are annealed between  $T_g$ , at low temperatures, and the temperature of phase separation, or  $T_d$ , at high temperatures. This temperature gap varies with PMMA tacticity and composition of the blends and is comprised within 20–40 K for PVC/PMMA blends, 10–50 K for CPVC/PMMA blends, and 10–130 K for Saran/PMMA blends.

Temperatures of phase separation have been obtained, in the literature, by various methods such as optical microscopy and light scattering. These methods are appropriate when there is a fair difference in refractive index between the polymers involved or when the size of the dispersed phase is large enough to scatter a significant amount of light. They have been shown to be most useful with, for example, mixtures of poly(styrene) (PS) and poly(vinyl methyl ether) (PVME)<sup>29</sup> where the refractive indexes ( $n$ ) of the pure components at 293 K are 1.590 and 1.466, respectively. However, numerous attempts to apply these methods with PVC/PMMA, CPVC/PMMA, and Saran/PMMA blends have given no results which can be partly related to a small refractive index difference between PVC ( $n = 1.540$ ) and PMMA ( $n = 1.495$ ) which does not allow a satisfactory estimation of the cloud-point curve.<sup>30</sup> The DSC method used in this paper to detect  $T_d$ 's is certainly more tedious than these other methods, but it is at the same time more sensitive since it cannot only detect the  $T_g$  but also detect the beginning of phase separation long before it is macroscopically evident through turbidity measurements.<sup>31</sup>

This latter advantage might explain the fact that, in some cases, the  $T_d$ 's measured by DSC are slightly lower than the LCSTs reported in the literature. For instance, Woo et al.<sup>21</sup> studied blends of a Saran with three PMMA's, one of them being isotactic while the two others were

**Table VI**  
Miscibility Behavior of Chlorinated Polymer/Poly(methyl methacrylate) Blends after Annealing at 423 K for 3 Min<sup>a</sup>

	PMMA	Saran	PVC	CPVC
ISO-1			I	
ISO-2	M		I	I
ISO-3	M		M	I
ISO-4	M		M	I
ATA-1	M		M	I
SYN-1	I		M	M
SYN-2	I		M	M
SYN-3	I		M	M
SYN-4	I		M	M

<sup>a</sup> Abbreviations: I, immiscible; M, miscible.

atactic. They observed a cloud-point curve occurring in the vicinity of 440–460 K for Saran/isotactic PMMA in agreement with the average temperature of phase separation of Saran/ISO-2 blends reported herein at 453 K. However, the average  $T_d$  of 433 K that we obtained for Saran/ATA-1 blends is low comparatively to the cloud-point curve of Saran/atactic PMMA blends reported by these authors that appears between 450 and 500 K. This discrepancy might not only be related to differences in sensitivity of the two methods but also to slight differences in the copolymer composition and methods of preparation of blends.

Table VI summarizes the miscibility behavior of the 25 chlorinated polymer/PMMA blends investigated in this work after annealing at 423 K. According to the single- $T_g$  criterion, 15 of them were found to be miscible. It is clear from this table that the choice of a particular thermal treatment for these blends normally leads to miscibility of a fraction of the mixtures, except if the thermal treatment is done below 368 K, which is the lowest  $T_d$  recorded that would lead to the miscibility of each blend. Table VI also gives an indication of the importance of the microstructure of PMMA toward the phase behavior of chlorinated polymer/PMMA blends, the selection of a proper thermal treatment becoming somehow arbitrary if the tacticity of the PMMA used in preparing a blend is not known.

The influence of the tacticity of PMMA is clearly illustrated in Figure 3. The substitution of syndiotactic PMMA for isotactic PMMA in PVC/PMMA blends raises the LCST of the blend by about 70 K while a similar substitution in CPVC/PMMA blends increases the LCST of the blend by nearly 50 K. On the other hand, such a substitution in Saran/PMMA blends results in a decrease of the LCST by almost 50 K. Thus, Figure 3 enables one to predict the phase behavior of a chlorinated polymer/PMMA blend providing that the microstructure, the chlorine content, and the thermal history of the blend are known. However, Figure 3 does not provide any information on the effects of molecular weight and polydispersity. Nevertheless, the influence of these parameters is rather well-known,<sup>32–34</sup> they should not strongly influence the general trends observed as a function of microstructure; however,  $T_d$ 's are expected to decrease with molecular weight such that lower molecular weights should increase the miscibility gaps reported herein. For instance, an increase in molecular weight of isotactic PMMA from 8000 to 17500 decreases the LCST of a PVC/PMMA blend from 453 to 443 K.<sup>24</sup>

The phase separation seen in each of these chlorinated polymer/PMMA mixtures can be explained by a variation of the thermodynamic interaction parameter  $\chi$  which becomes positive above the LCST. According to Patterson,<sup>35,36</sup>  $\chi$  can be expressed by two contributions: an in-

teractional contribution which is associated with the contact-energy dissimilarity between the components and a free-volume contribution which follows from a difference in the thermal expansion of the compounds. Phase separation takes place on raising the temperature of a blend because the free volume contribution becomes more positive and the interactional contribution is less negative owing to the dissociation of the specific interactions that are, in part, responsible for the miscibility of most polymers. Therefore, the observation of a phase separation with an increase of the temperature can be related to a balance of these two contributions.

Miscibility between chlorinated polymers and PMMA is then due, in part, to the presence of specific interactions between these two series of polymers. These specific interactions must be sufficiently strong to counteract the intramolecular hydrogen bonding between chlorinated polymer chains and the self-aggregation occurring in syndiotactic PMMA under proper conditions.<sup>37,38</sup> The nature of these specific interactions have been thoroughly discussed in previous papers related to the miscibility behavior of chlorinated polymers blended with polyesters or polymethacrylates.<sup>5,7,11,16</sup> It was then suggested that hydrogen-bonding interactions involving either the  $\alpha$ -hydrogen or the  $\beta$ -hydrogen atoms of the chlorinated polymers and the carbonyl groups of PMMA were competing along with dipole-dipole interactions between the Cl—C—Cl and C=O groups so as to ensure miscibility. A minimum chlorine content of the chlorinated polymer is a necessary requirement to favor such specific interactions and, therefore, miscibility.

This approach complements nicely the interpretation of Walsh and Cheng,<sup>17</sup> who consider dispersive forces overwhelmed by specific interactions as contributors to the heat of mixing. A third approach<sup>39</sup> indicates that polymers may be miscible even when none of the interaction parameters between individual units is negative; thus an exothermic heat of mixing can be obtained if the repulsive intramolecular interactions from the subunits compensate unfavorable intermolecular contacts.<sup>40</sup>

Unfortunately, these models do not take into account the influence of tacticity upon miscibility. However, the importance of this parameter has been outlined by Balazs et al.,<sup>41</sup> who introduced chemical triad sequence distributions in their model. A variation of tacticity of the PMMA chain influences its flexibility and the chemical environment of the chlorinated polymer chain in the blends. So, the difference in flexibility between the various tactic forms of PMMA has to be responsible for the difference in miscibility with chlorinated polymers as was proposed by Vorenkamp et al.<sup>24</sup> Different methods were applied to study the various tactic forms of PMMA,<sup>42–44</sup> and all show that the flexibility of the isotactic chain is greater than that of the syndiotactic chain which must be related to the fact that isotactic PMMA has a conformation of lowest energy corresponding to a 10/1 helix having a pitch of 21.1 Å while syndiotactic PMMA shows an all-trans conformation with torsion angles that accentuate the curvature of the syndiotactic sequence.<sup>45–48</sup> With use of Flory's equation of state theory, this difference in chain flexibility can be related to differences in free volume between the different tactic forms of PMMA and the chlorinated polymer, as done by Vorenkamp et al.<sup>24</sup>

This paper describes the evolution of the phase behavior of chlorinated polymer/PMMA blends as a function of tacticity and chlorine content. A more theoretical study is currently under way so as to predict this phase behavior by modeling the respective contributions of the chlorine

content in the chlorinated polymers and the stereoregularity in PMMA toward miscibility.

**Acknowledgment.** R.J. and P.T. thank the "Services de la programmation de la politique scientifique" (Brussels) for financial support. R.F. is indebted to IRSIA for a fellowship that supported her Ph.D. Thesis. R.E.P. thanks the National Sciences and Engineering Research Council of Canada and the Department of Education of the Province of Quebec (FCAR program) for the financial support of his part of this study. This work was made possible by a Quebec-Belgique grant provided by "la communauté française de Belgique" and the Department of Education of the Province of Quebec.

**Registry No.** ISO, 25188-98-1; ATA, 9011-14-7; PVC, 9002-86-2; (vinyl chloride)(vinylidene chloride) (copolymer), 9011-06-7.

## References and Notes

- (1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978.
- (2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979.
- (3) Walsh, D. J.; Higgins, J. S.; Maconnachie, A. *Polymer Blends and Mixtures*; Martinus Nijhoff: The Netherlands, 1985; NATO ASI Series E, Applied Sciences No. 89.
- (4) Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* 1981, 22, 918.
- (5) Prud'homme, R. E. *Polym. Eng. Sci.* 1982, 22, 90.
- (6) Woo, E. M.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* 1983, 28, 1347.
- (7) Aubin, M.; Bédard, Y.; Morrissette, M.-F.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* 1983, 21, 233.
- (8) Aubin, M.; Prud'homme, R. E. *Polym. Eng. Sci.* 1984, 24, 350.
- (9) Coleman, M. M.; Zarian, J. J. *Polym. Sci., Polym. Phys. Ed.* 1979, 17, 837.
- (10) Varnell, D. F.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. *Polym. Eng. Sci.* 1983, 23, 658.
- (11) Garton, A.; Cousin, P.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* 1983, 21, 2275.
- (12) Walsh, D. J.; Higgins, J. S.; Chai, Z. *Polymer* 1982, 23, 336.
- (13) Chai, Z.; Sun, R.; Walsh, D. J.; Higgins, J. S. *Polymer* 1983, 24, 263.
- (14) Walsh, D. J.; McKeown, J. G. *Polymer* 1980, 21, 1330.
- (15) Razinskaya, I. N.; Vidyakina, L. I.; Radbil', T. I.; Shtarkman, B. P. *Polym. Sci. USSR (Engl. Transl.)* 1972, 14, 1079.
- (16) Tremblay, C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* 1984, 22, 1857.

- (17) Walsh, D. J.; Cheng, G. L. *Polymer* 1984, 25, 499.
- (18) Schurer, J. W.; de Boer, A.; Challa, G. *Polymer* 1975, 16, 201.
- (19) Vanderschueren, J.; Janssens, A.; Ladang, M.; Niezette, J. *Polymer* 1982, 23, 395.
- (20) Albert, B.; Jérôme, R.; Teyssié, P.; Smyth, G.; Boyle, N. G.; McBrierty, V. J. *Macromolecules* 1985, 18, 388.
- (21) Woo, E. M.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Symp.* 1984, 71, 137.
- (22) Walsh, D. J.; Shi, L.; Chai, Z. *Polymer* 1981, 22, 1005.
- (23) Jager, H.; Vorenkamp, E. J.; Challa, G. *Polym. Commun.* 1983, 24, 290.
- (24) Vorenkamp, E. J.; ten Brinke, G.; Meijer, J. G.; Jager, H.; Challa, G. *Polymer* 1985, 26, 1725.
- (25) Goode, W. E.; Owens, F. H.; Fellmann, R. P.; Snyder, W. H.; Moore, J. E. *J. Polym. Sci.* 1960, XLVI, 317.
- (26) Ramey, K. C. *J. Polym. Sci., Part B* 1967, 5, 859.
- (27) Tremblay, C. M.Sc. Thesis, Université Laval, 1983.
- (28) Kaplan, D. S. *J. Appl. Polym. Sci.* 1976, 20, 2615.
- (29) Voigt-Martin, I. G.; Leister, K.-H.; Rosenau, R.; Koningsveld, R. *J. Polym. Sci., Polym. Phys. Ed.* 1986, 24, 723.
- (30) Hemsley, D. A. *The Light Microscopy of Synthetic Polymers*; Oxford University: New York, 1984.
- (31) Lau, S.; Pathak, J.; Wunderlich, B. *Macromolecules* 1982, 15, 1278.
- (32) Flory, P. J. *J. Am. Chem. Soc.* 1965, 87, 1833.
- (33) McMaster, L. P. *Macromolecules* 1973, 6, 760.
- (34) Roe, R.-J.; Lu, L. *J. Polym. Sci. Polym. Phys. Ed.* 1985, 23, 917.
- (35) Patterson, D.; Robard, A. *Macromolecules* 1978, 11, 690.
- (36) Patterson, D. *Polym. Eng. Sci.* 1982, 22, 64.
- (37) Spěvák, J.; Schneider, B.; Dybal, J.; Stokr, J.; Baldrian, J.; Pelzbauer, Z. *J. Polym. Sci., Polym. Phys. Ed.* 1984, 22, 617.
- (38) Dybal, J.; Spěvák, J.; Schneider, B. *J. Polym. Sci., Polym. Phys. Ed.* 1986, 24, 657.
- (39) Paul, D. R.; Barlow, J. W. *Polymer* 1984, 25, 487.
- (40) Pfennig, J.-L. G.; Keskkula, H.; Barlow, J. W.; Paul, D. R. *Macromolecules* 1985, 18, 1937.
- (41) Balazs, A. C.; Sanchez, I. C.; Epstein, I. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1985, 18, 2188.
- (42) Shindo, H.; Murakami, I.; Yamamura, H. *J. Polym. Sci., Polym. Chem. Ed.* 1969, 7, 297.
- (43) Edzes, H. T.; Veeman, W. S. *Polym. Bull.* 1981, 5, 255.
- (44) Quach, A.; Wilson, P. S.; Simha, R. *J. Macromol. Sci. Phys.* 1974, B9, 533.
- (45) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* 1976, 9, 531.
- (46) Bosscher, F.; ten Brinke, G.; Eshuis, A.; Challa, G. *Macromolecules* 1982, 15, 1364.
- (47) Vacatello, M.; Flory, P. J. *Macromolecules* 1986, 19, 405.
- (48) Sundararajan, P. R. *Macromolecules* 1986, 19, 415.

## Polymorphism in a Liquid Crystalline Polyester Based on 4,4'-Biphenol, Terephthalic Acid, and *p*-Hydroxybenzoic Acid (1:1:2)

N. D. Field,\* R. Baldwin, R. Layton, P. Frayer, and F. Scardiglia

Dartco Manufacturing Inc, P.O. Box 5867, Augusta, Georgia 30906.

Received October 9, 1988

**ABSTRACT:** The polyester from 1 mol of 4,4'-biphenol, 1 mol of terephthalic acid, and 2 mol of *p*-hydroxybenzoic acid, synthesized by the acidolysis condensation reaction of the acetylated mixture, was studied by using wide-angle X-ray diffraction and differential scanning calorimetry (DSC). X-ray diffraction demonstrated a reversible crystal-crystal transition at about 100 °C. The transition was also observed with DSC as a small endotherm. The most prominent calorimetric feature is an endotherm at about 427 °C corresponding to the crystal-nematic transition. There is also a small endotherm at about 472 °C which may correspond to the nematic-isotropic transition. On cooling from 450 °C at 10 deg/min, there is observed about 40 deg of supercooling before crystallization occurs. Further cooling proceeds through the crystal-crystal transition. Rapid cooling from the melt produces a quenched solid which does not demonstrate the crystal-crystal transition. Annealing at elevated temperatures converts this metastable form to one which does demonstrate the reversible crystal-crystal transition.

## Introduction

Thermotropic liquid crystalline polymers are of considerable interest, not only from a theoretical but also from a commercial point of view. Of special interest are completely aromatic polyesters wherein the connecting linkages are all para. These have high melting points, exhibit liquid crystalline properties in the melt, and demonstrate very high moduli in fabricated form. This paper will deal with the polymer from 4,4'-biphenol (BP), terephthalic acid (TA), and *p*-hydroxybenzoic acid (PHBA) in the molar ratio 1:1:2.

Earlier papers described a 1:1:2 polymer made by heating the acetates of BP and PHBA with TA in an inert, high-boiling liquid.<sup>1-3</sup> The molecular weight of the polymer was increased by further heating under vacuum at 320-340 °C, accompanied by raising of the melting point. The polymer was reported as having a melting point of around 430 °C, as measured by differential scanning calorimetry (DSC), with an endotherm of about 17 J/g. Low molecular weight polymer readily crystallized from the melt. High molecular weight polymer, on the other hand, did not show an exotherm on cooling from the melt at a rate of 10 deg/min, i.e., no tendency to crystallize. Polymer, quenched from the melt after shearing, exhibited high birefringence. No evidence for any other transition was presented. Solution properties could not be measured for lack of a solvent.

Wide-angle X-ray measurements disclosed reflections at 4.5 (vs), at 3.9 (s), and at 4.2 Å (w). The 4.5 spacing was attributed to the distance between chains. The supercooled form also displayed a peak at 4.5 Å but of appreciably less intensity and substantially broadened. Measurements, utilizing <sup>13</sup>C NMR, located the PHBA-derived protons in two regions, one more ordered than the other. This was interpreted as demonstrating that the polymer sequence distribution was of a blocky nature.

## Experimental Section

The 1:1:2 polyester was prepared by methods reported in the literature.<sup>4-6</sup> To summarize, 1 mol of BP, 1 mol of TA, 2 mol of PHBA, and excess acetic anhydride were refluxed to assure acetylation, in situ, of the phenolic hydroxyl groups. The slurry temperature was gradually raised with simultaneous distillation

to remove the acetic acid formed in the acetylation reaction as well as that formed in the acidolysis polymerization reaction.

Melt polymerization was continued until an oligomer of 2000-3000 number-average molecular weight was formed. The melt was then cooled to a solid which was ground to a powder. Polymerization, in the solid state, was then continued under a nitrogen sweep until high molecular weight was attained as indicated by DSC. The number-average molecular weight of the polymer of this study is estimated from end group analysis to be about 25 000.

Diffractometer data were recorded in the reflection mode by using a Philips PN 3550 diffractometer equipped with a Paar HKT high-temperature attachment and a Philips XRG-3000 X-ray generator. A nitrogen atmosphere was used. A copper X-ray tube was used at 40 kV and 30 mA, and the K $\alpha$  line was isolated by a curved graphite monochromator. Diffractometer angle, sample temperature, and data acquisition were programmed by means of an IBM PC-XT equipped with a Keithley System 570 data acquisition workstation and a centroid motion controller. All software was written in-house for this application. Wide-angle X-ray diffraction photographs were obtained with a flat film camera using Kodak Direct Exposure Film on the Philips XRG-3000 X-ray generator.

DSC determinations were made utilizing a Du Pont 1090 instrument.

## Results

**DSC Determinations.** In order to minimize the effect of the previous thermal history, as-synthesized polymer was heated in the DSC apparatus to 450 °C at 20 deg/min, under nitrogen, followed by cooling at 10 deg/min. The specimen was then subjected to a second heating/cooling cycle and the data were plotted. Results are shown in Figure 1. The most prominent features of the heating scan are the small endotherm at around 100 °C with an enthalpy change of around 2 J/g and the appreciably larger one at 427 °C with an enthalpy change of about 10.5 J/g. Cooling from 450 °C, at 10 deg/minute, resulted in supercooling of about 40 deg, the exotherm starting at about 384 °C. Cooling at a controlled rate below the indicated temperature cutoff was difficult in our apparatus, but, nevertheless, it was apparent from other data that the lower temperature transition on cooling resulted in a small exotherm. Figure 2 shows the result of heating to 530 °C. A small endotherm, with an enthalpy change of about 1.5 J/g, appears at about 472 °C, indicating a third transition. This is followed by extensive decomposition.

**Wide-Angle X-ray Diffraction.** Flat plate powder diagrams (Figure 3), on the as-synthesized material, re-

\* To whom correspondence should be addressed at Elkins Park Polymer Associates, 373 Linden Drive, Elkins Park, PA 19117.