Lyotropic Block Copolymers of Poly(*p*-benzamide) and Poly(terephthalamide of *p*-aminobenzhydrazide): The Ternary System Copolymer/Poly(*p*-benzamide)/Dimethylacetamide–Lithium Chloride

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Received February 5, 1991; Revised Manuscript Received July 10, 1991

ABSTRACT: A rod–coil diblock copolymer has been synthesized by the coupling reaction between end groups of the rod- and coillike homopolymers. Namely, poly(*p*-benzamide) (PBA) and poly(terephthalamide of *p*-aminobenzhydrazide) (PABH-T) have been considered as constituents of the rigid and flexible blocks, respectively. The phase diagram of a PBA/copolymer mixture in the presence of a diluent has been determined and compared with the predicted behavior, based on Matheson–Flory theory. From a qualitative point of view, the agreement is quite good, while it is only partial on a quantitative basis. This latter point is discussed in detail in terms of copolymer molecular parameters, as well as in terms of limited correspondence of the model to the experimental system.

Introduction

Rod–coil copolymers, composed of two or three blocks, represent useful model compounds which have attracted relevant theoretical interest[1–3] and some consideration of their potential applications.[3–7] If the rigid block is soluble and chemically compatible with the flexible one, lyotropic behavior is expected. This situation was first described theoretically by Matheson and Flory:[1] the copolymer is predicted to give a nematic phase at a limit concentration (c_p'), which is higher than that observable for rods having the same length as the rigid block. Moreover, c_p' increases as the flexible chain becomes longer. The above theory[1] also takes into account the behavior of athermal ternary mixtures of the copolymer with the rigid homopolymer and a common solvent: by increasing the overall concentration of the polymeric components, solutions are first isotropic, then biphasic (plus a triphasic region in the case of long flexible block), and finally anisotropic. It is remarkable that the flexible chains should enter the mesophase at high concentrations.

Halperin[3] has recently dealt with the aggregation behavior of rod–coil copolymers in the presence of a selective solvent for the coil block. The equilibrium structures (micelles and lamellae) were analyzed, also by taking into account the chemical compatibility between the blocks. These micelles are composed of an internal core containing the rods and an external starlike corona, while lamellae have been predicted to form smectic phases.

Despite these theoretical investigations, very few experimental data have been available so far. Moreover, the majority of the synthetic approaches have been performed in order to produce reinforcing materials, disregarding phase properties.

Poly(*p*-phenylene terephthalate) and some derivatives carrying substituents on the aromatic ring, poly(*p*-benzamide) (PBA) and poly[(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)-1,4-phenylene], are the rigid blocks most widely employed, while aliphatic and aromatic polyamides as well as polymers based on benzimidazole or benzothiazole are the most used flexible blocks.[4–6,8–11]

Block copolymers of PBA and poly(terephthalamide of *p*-aminobenzhydrazide) (PABH-T), where PABH-T can be considered the "flexible" block as compared to the rigid PBA, are very useful models for testing the theoretical prediction, being chemically compatible[12] and soluble in dimethylacetamide–LiCl mixtures (DMAc–LiCl).

The first synthetic attempt was performed by Krigbaum et al.,[13] using Yamazaki et al.'s phosphorylation reaction.[14] Phase properties have been examined also in collaboration with our research group,[15,16] and the formation of a mesophase containing short PABH-T chains has been assessed. However, due to the very low copolymer yield, probably intrinsic to the synthetic procedure, as later demonstrated,[17] it has been impossible to give a complete description of the phase behavior of that system. More recently,[18] we have applied a new synthetic method, based on the coupling reaction between preformed PBA and acyl chloride monoterminated PABH-T. The method gives a good copolymer yield and allows an a priori choice of the flexible block length.

In this paper, we present the ternary phase diagram of the system PBA/copolymer/DMAc–3% LiCl, starting from a PBA/copolymer mixture of about a 1:1 w/w ratio.

The isotropic, biphasic, and anisotropic regions have been characterized. It has also been demonstrated that PABH-T flexible blocks, even with relatively high molecular weights, do enter the nematic phase.

Experimental Section

Materials and Methods. p-Aminobenzhydrazide (PABH), terephthaloyl chloride (TC), DMAc, dimethyl sulfoxide (DMSO), and LiCl were treated according to previously described procedures.[18]

Solution viscosity, polarizing optical microscopy, and vapor pressure osmometry measurements, as well as UV spectral measurements, were performed according to methods already utilized.[12,18]

Chromatograms of PBA/PABH-T and PBA/copolymer mixtures were obtained using a Beckman liquid chromatograph apparatus, equipped with a UV detector and interfaced with an IBM PS2-50 data station. The standard column size was 4.6 mm × 4.5 cm, and the stationary phase was based on Beckman C18 ultraspheres. Methanol was used as a mobile phase in order to precipitate the polymeric components. The latter were first eluted by using a gradient of methanol and DMAc, with a DMAc

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0024-9297/91/2224-6578$02.50/0

Table I
Homopolymer Characteristics

homopolymer	$[\eta]$, dL/g	M_w	M_n	c_p'
PBA	1.67[a]	12150	7500	5.6[c]
PABH-T	0.84[b]	8000	4700	

[a] In H_2SO_4 at 25 °C. [b] In DMSO at 25 °C. [c] In DMAc–3% LiCl.

Table II
Characterization Data of a PBA/Copolymer Stock Sample

wt increment, %	PABH-T linked (w/w), %	copolym (w/w), %	$[\eta]$, dL/g
17.6	15	36	3.1

content progressively increasing from 0 to 100%. Then, a second gradient of DMAc and DMAc–3% LiCl was applied in order to complete the components' elution.

PBA and PABH-T Homopolymer: Synthesis and Characterization. The sample of PBA used was of the same stock employed in a previous work.[18] M_w and M_n were determined by measurement of the intrinsic viscosity in H_2SO_4 at 25 °C[19] and by titration of –COOH terminal groups, respectively[17] (see Table I). The critical concentration c_p' at which the anisotropic phase appears was determined by polarizing optical microscopy in DMAc–3% LiCl, as previously described.[12]

Acid chloride monotherminated PABH-T was prepared according to Dvornic's[20] procedure. M_w was determined by measuring the intrinsic viscosity in DMSO at 25 °C,[21] while M_n was obtained by vapor pressure osmometry.[18]

Table I collects the characterization data of the two homopolymers.

PBA–PABH-T Copolymer: Synthesis and Preliminary Characterization. The copolymer synthesis was performed according to the method previously described,[18] with the optimization of some experimental conditions. The product, precipitated from the reaction batch, is a mixture of PBA and PABH-T unreacted homopolymers plus a certain amount of copolymer, which, according to the chosen conditions, should be a diblock material.[18] Unreacted PABH-T was extracted with hot DMSO. As previously demonstrated for mechanical blends of the same homopolymers, the extraction is quantitative.[12] Therefore, the residue is only a mixture of unreacted PBA and PBA–PABH-T copolymer (called stock sample in the following). As explained later, its composition was evaluated by different methods.

Table II shows some characteristics of the PBA/copolymer mixture used to obtain the ternary phase diagram. The first column reports the weight increase of the mixture with respect to the amount of pure PBA used in the synthesis. It constitutes a first indication that some PABH-T has been linked to PBA. The second column gives the percent of PABH-T calculated from the weight increment. By taking into account the M_n ratio of the two homopolymers and assuming a two-block structure, it is possible to calculate the copolymer content in the final blend (disregarding any chain length effect on preferential coupling between the two homopolymers). This value has been reported in the third column. The last column gives the intrinsic viscosity of the stock sample in DMAc–3% LiCl.

Phase Diagram. Three solutions, at an overall polymer concentration c_p between 7.5 and 9.2% (w/w), were prepared by dissolving known amounts of the stock material in DMAc–3% LiCl. In order to get equilibrium conditions, the solid was added and dissolved little by little, until the final concentration was reached. The samples were kept under slow stirring at room temperature for at least 2 weeks. All samples were biphasic. Phase separation was obtained by centrifugation at 30 000 rpm for 30 h. Subsequent precipitation by water, followed by washing, drying, and UV analysis, gave the overall concentration of the polymeric material and the content of linked PABH-T in each phase.

The overall polymer composition is also expressed as volume fraction v_p, to facilitate comparison with theory. In order to calculate v_p, we need to know the specific volumes V_{sp} of homopolymers, copolymer, and solvent.

The following values of V_{sp} at 25 °C were used: $V_{sp,PBA} = 0.754$ mL/g, $V_{sp,PABH\text{-}T} = 0.697$ mL/g, $V_{sp,DMAc\text{-}3\%LiCl} = 1.036$ mL/g.[12]

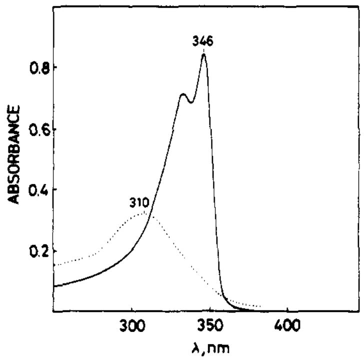

Figure 1. UV absorption spectra of PBA (continuous line) and PABH-T (dotted line) in DMAc–3% LiCl. $c_p = 0.037$ mg/mL.

Table III
Spectroscopic Constants (mL/mg)

$K_{310,PBA}$	$K_{310,PABH\text{-}T}$	$K_{346,PBA}$	$K_{346,PABH\text{-}T}$
7.836	8.121	23.440	2.941

For the copolymer, V_{sp} was calculated by assuming both the additivity of contributions from the two blocks and a ratio between the weights of the rod and coil blocks equal to the ratio of the corresponding M_n values (see Table I). The latter assumption was also used to transform the percent of PABH-T (4th, 8th, and 13th columns of Table IV) into copolymer percent, as indicated above. Intrinsic viscosities of the recovered material (three samples from isotropic solutions and three from the anisotropic ones) were measured in DMAc–3% LiCl at 25 °C.

Results and Discussion

From the data of Table II it can be noticed that $[\eta]$ in DMAc–3% LiCl is 3.1 dL/g, which, as compared to 2.42 for PBA homopolymer and 0.84 for PABH-T, is a further indication in favor of some copolymer formation.

In order to confirm this result, we have studied the spectroscopic behavior of PBA and PABH-T in the UV absorption region.

Figure 1 reports the UV spectra of PBA (continuous line) and PABH-T (dashed line) solutions, at the same concentration. PBA and PABH-T show the maximum absorbance at $\lambda = 346$ and 310 nm, respectively. By assuming absorbance additivity rules, for both mechanical blends and copolymers, it is possible to write a system of two equations at two different wavelengths (310 and 346 nm)

$$A_\lambda = K_{\lambda,PBA} c_{PBA} + K_{\lambda,PABH\text{-}T} c_{PABH\text{-}T} \tag{1}$$

where c are the concentrations expressed in mg/mL and K_λ are constants, measured by using solutions of PBA and PABH-T at known concentrations.

The results are collected in Table III.

By using these values, errors in composition are less than 10% when the PABH-T content is higher than 20% and increase at lower concentrations. By applying the above method to the stock sample, we have obtained $A_{310}/A_{346} = 0.40$, which corresponds to a PABH-T content of ca. 19% (w/w), equivalent to 46% (w/w) in terms of a two-block copolymer. This value is somewhat higher than that obtained from the weight increment (see Table II). However, it should be considered that the latter evaluation probably suffers from some material loss during precipitation, extraction, and washing steps. Therefore, it is the higher value that has been chosen to outline the ternary diagram.

Stronger evidence of copolymer formation was further obtained by high-performance precipitation liquid chromatography (HPPLC). In this method, a dilute solution of the polymeric blend is injected at the top of the column

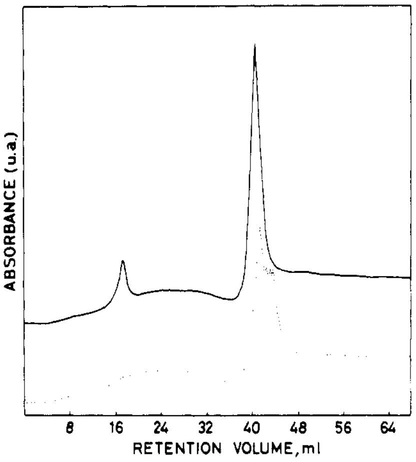

Figure 2. HPPLC chromatogram of a mechanical blend of PBA and PABH-T (continuous line) and PBA/copolymer stock sample (dotted line).

and polymer precipitates onto the stationary phase. At this point the components can be separated by a suitable solvent pair gradient using the conditions described in the Experimental Section. The results are reported in Figure 2. The continuous line corresponds to the chromatogram of the mechanical blend containing 19 and 81% of PABH-T and PBA, respectively. The first peak is related to the free PABH-T and the second one to the free PBA. The dotted line corresponds to the chromatogram of the PBA/copolymer stock sample. It is evident that the peak of free PABH-T is absent, whereas PBA and the copolymer merge together in the second peak.

We can therefore conclude that PABH-T, observed by UV spectroscopy, does not belong to free homopolymer but is effectively linked in the copolymer.

Consequently the stock sample can be used to study the phase behavior of the PBA/copolymer mixture in DMAc–3% LiCl according to the procedure previously described. Table IV collects the experimental results; v_p values (columns 3, 7, and 12) have been used to construct the ternary diagram (Figure 3). Subscripts 1–3 indicate solvent, PBA, and copolymer, respectively, and p the overall polymeric (PBA + copolymer) content.

The scales of the lateral sides represent the binary systems PBA/solvent and copolymer/solvent (left and right sides, respectively), while the horizontal side gives the volume fraction of the copolymer divided by the combined volume fractions of PBA and copolymer ($v_3/(v_2 + v_3)) \times 100$. It can easily be observed that the experimental points separate the area of the diagram into three regions. At low overall v_p, isotropic solutions are stable; i.e., PBA and copolymer coexist in a homogeneous phase which goes from the top (pure solvent) to the v_p' line. This line tends to bend toward higher v_p' values as the copolymer content increases, with a trend which is similar to that observed for rod–coil mechanical blends.[12]

Under the v_p' line a biphasic region appears. It should be limited in the low part of the diagram by the v_p'' curve (limit of stability of the isotropic phase). However, the relatively low solubility of the polymeric mixture hampers the complete analysis of the biphasic gap, and only a short v_p'' segment on the left side of the diagram is experimentally accessible. Finally, a third region, corresponding to the area between the v_p'' line and the left axis on the figure, represents the anisotropic region where PBA and copolymer coexist.

The maximum copolymer content (ca. 80%) has been found for the isotropic phase of sample C. Any attempt to increase that content, for example, by dissolving the material recovered from the three isotropic solutions at $v_p > 0.06$ and performing a further separation, was unsuccessful as the new conjugated anisotropic phase crystallized.

The average copolymer content of the aforementioned recovered material was 68%, and its c_p', determined by polarizing optical microscopy, was 6%. The latter value, together with those of PBA and the initial stock sample, has been transformed into volume fraction, and the corresponding values (0.051, 0.041, and 0.044, respectively) are reported in Figure 3.

The general trend of Figure 3 is qualitatively in line with theoretical predictions.[1] In order to perform a more quantitative comparison, the axial ratio of PBA, x_2, and the ratio between the contour length and the diameter of the copolymer, L_3, must be established. As far as x_2 is concerned, we may recall that values larger than expected on the basis of the persistence length have already been observed for PBA/diluent systems.[22,23] Moreover, in order to have the best fit of the experimental results, it was suggested to derive x_2 from the v_2' experimental value and eqs C2–C6 of ref 24. $x_2 = 200$ was obtained for our PBA sample.

L_3 is the sum of two terms. The first one is related to the rigid block ($\equiv x_2$), while the second refers to the flexible block ($\equiv x_3$). Two main routes have been suggested and already applied for x_3 calculation. According to the first one, x_3 is derived from the ratio of the contour length and the chain diameter, obtained from the polymer density.[24] Alternatively, x_3 is deducible from the ratio between the molar volume of the polymer and that of the diluent.[23] $x_3 = 92$ and $x_3 = 62$, respectively, are the values obtained for the PABH-T block by using the chain parameters, density, and molar volume of PABH-T.[23]

If the above x_3 values are used in order to determine v_p' for a rod–coil mechanical mixture,[12] two curves coincident within the experimental error would be obtained (we recall that the v_p'' line would in any case be coincident with the PBA/diluent axis). However, we are dealing now with a rod/copolymer/diluent ternary mixture, and a strong influence of x_2 and x_3 on the phase diagram is theoretically predicted.[1]

Figure 4a gives the phase diagram calculated by using $x_2 = 200$ and $x_3 = 62$. The positions of v_2', v_2'', v_3', and v_3'' for the binary PBA/diluent and copolymer/diluent systems are shown. Biphasic ternary mixtures lie in the area between the v_p' and v_p'' curves. Below v_p'' a unique anisotropic phase is stable.

A more complex diagram, related to the pair of values $x_2 = 200$ and $x_3 = 92$, is shown in Figure 4b. In this case v_3' and v_3'' are shifted toward higher values, although the left part of the v_p' curve is substantially coincident with that of Figure 4a. More dramatic is the change of v_p'' trend. The area of the anisotropic phase is considerably reduced, and a triphasic area (shown in part in the figure) appears. Parts a and b of Figure 4 also contain the experimental v_p' and v_p'' values of the ternary blends.

It is easily observed that experimental results concerning v_p' are in good agreement with both theoretical curves. The only possibility of discrimination between the two situations (i.e., between x_3 values) would be a direct determination of the biphasic gap for the binary system copolymer/diluent. However, the difficulties concerning PBA/copolymer mixture separation, previously described, hamper this experiment.

On the other hand, experimental points representing v_p'' lie in an intermediate position between the two theoretical curves. With respect to Figure 4a, experimental results seem to indicate a different trend of v_p'' and a wider extension of the biphasic gap. The opposite is valid in the case of Figure 4b, where experimental results support

Table IV
Summary of Data for a PBA/Copolymer/Diluent[a] System

					isotropic phase					anisotropic phase				
sample	ρ_p (w/w), %	v_p[b]	PABH-T (w/w), %	copolym (v/v), %	ρ_p (w/w), %	v_p[b]	PABH-T (w/w), %	copolym (v/v), %	[η], dL/g	ρ_p (w/w), %	v_p[b]	PABH-T (w/w), %	copolym (v/v), %	[η], dL/g
A	7.49	0.055	19	46	6.55	0.048	26	63	2.25	10.23	0.076	8	19	3.7
B	8.27	0.061	19	46	6.85	0.049	30	73	2.1	10.67	0.079	7	18	3.5
C	9.16	0.068	19	46	7.47	0.053	32	78	1.9	11.35	0.085	7	18	3.2

[a] DMAc–3% LiCl. [b] $v_p = v_2 + v_3$.

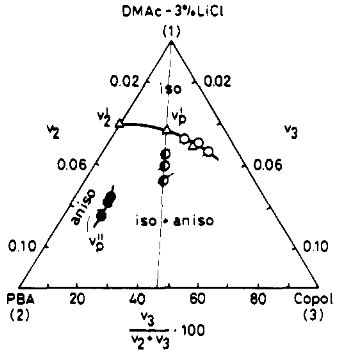

Figure 3. PBA/copolymer/DMAc–3% LiCl ternary phase diagram: (◐) overall composition of the biphasic mixture; (○ and ●) compositions of conjugated isotropic and anisotropic phases, respectively; (▲) v_p' determined by polarizing optical microscopy.

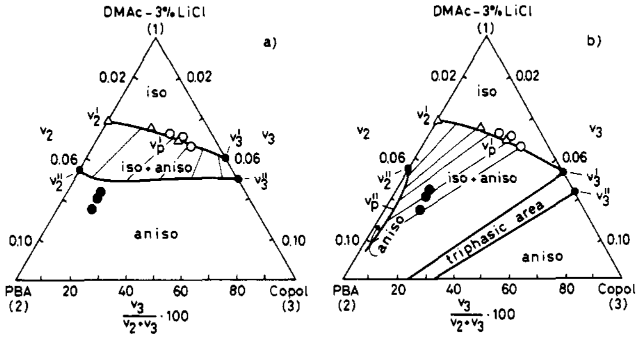

Figure 4. Theoretical phase diagram for the athermal system rod/rod–coil/diluent. Axial ratio of rod $x_2 = 200$; contour length of the flexible block $x_3 = 62$ (a) and $x_3 = 92$ (b), respectively (symbols for the experimental points, as in Figure 3).

a greater extension of the anisotropic region at the biphasic gap's expense. Unfortunately, saturation phenomena prevent experiments at higher v_p concentration also in this case. Moreover, we may observe that other factors could play an important role. First of all, we recall that theory[1] refers to athermal and monodisperse components. Our system, besides not being athermal,[23] is surely characterized by a high polydispersity degree, presumably enhanced by the coupling reaction between the two homopolymers, both polydisperse. A further point concerns the degree of flexibility of the PABH-T block, which is not as high as hypothesized for the theoretical model. At present, it is unknown whether a lower flexibility may help the entrance of the chain in the lyotropic nematic phase, although Yoon et al.[25,26] recently underlined the critical importance of highly extended conformers of flexible spacers in forming nematic thermotropic states. Finally we add a short comment about tie lines connecting conjugated phases inside the gap. According to theoretical predictions (Figure 4a,b), the experimental slope of the lines is coherent with a higher content of copolymer in the isotropic phase. Moreover, the intrinsic viscosity values, reported in Table IV, reveal that a significant portion of higher molecular weights is present in the anisotropic phase. This partition, already observed for pure PBA and its mixtures with flexible polymers,[12] probably also entails the copolymer, although the role played by the ratio between rigid and flexible blocks in a polydisperse sample has not yet been clarified.

In conclusion, we believe that, in spite of the uncertainty on the extension of the anisotropic area, present results clearly support the general features of the theory.[1] Moreover, the peculiar behavior of the lyotropic mesophase in accommodating a rod–coil copolymer composed on a coil block as long as 50% of the rigid one is conclusively demonstrated.

Acknowledgment. This research has been supported by CNR, the Italian Research Council, Progetto Finalizzato "Chimica Fine e Secondaria II". We are grateful to Mr. F. Pioli for his advice and expert technical assistance in carrying out HPPLC measurements.

References and Notes

(1) Matheson, R. R., Jr.; Flory, P. J. *Macromolecules* **1981**, *14*, 954.
(2) Huber, K. *Macromolecules* **1989**, *22*, 2750.
(3) Halperin, A. *Macromolecules* **1990**, *23*, 2724.
(4) Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai, T. *J. Macromol. Sci., Phys.* **1980**, *B17*, 591.
(5) Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.* **1986**, *32*, 6299.
(6) Martin, R.; Gotz, W.; Vollmert, B. *Angew. Makromol. Chem.* **1985**, *132*, 91.
(7) Prevorsek, D. C. In *Polymer Liquid Crystal*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic: New York, 1982.
(8) Wuang, H. H.; Chen, W. L. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1359.
(9) Takayanagi, M.; Goto, K. *J. Appl. Polym. Sci.* **1984**, *29*, 2057.
(10) Jadhav, J. Y.; Krigbaum, W. R.; Ciferri, A.; Preston, J. *J. Polym. Sci. (Lett.)* **1989**, *27*, 59.
(11) Tsai, T. T.; Arnold, F. E.; Hwang, W. F. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2838.
(12) Bianchi, E.; Ciferri, A.; Tealdi, A. *Macromolecules* **1982**, *15*, 1268.
(13) Krigbaum, W. R.; Preston, J.; Ciferri, A.; Zhan, S. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 653.
(14) Yamazaki, V.; Matzumoto, M.; Higaschi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373.
(15) Krigbaum, W. R.; Zhang, S.; Preston, J.; Ciferri, A.; Conio, G. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1043.
(16) Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A.; Krigbaum, W. R.; Preston, J. *Polym. J.* **1988**, *20*, 83.
(17) Conio, G.; Tealdi, A.; Russo, S.; Bianchi, E. *Polymer* **1990**, *31*, 362.
(18) Marsano, E.; Bianchi, E.; Conio, G.; Mariani, A.; Russo, S. *Polym. Commun.* **1991**, *32*, 45.
(19) Shaefgen, J. R.; Foldi, V. S.; Logullo, F. M.; Good, V. H.; Gulrich, L. W.; Killian, F. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1976**, *17*, 69.
(20) Dvornic, P. R. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1133.
(21) Burke, J. J. *J. Macromol. Sci., Chem. (A)* **1973**, *7*, 187.
(22) Ying, Q.; Chu, B. *Macromolecules* **1987**, *20*, 871.
(23) Bianchi, E.; Ciferri, A.; Conio, G.; Marsano, E. *Macromolecules* **1984**, *17*, 1526.
(24) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.
(25) Yoon, D. Y.; Brucker, S. *Macromolecules* **1985**, *18*, 651.
(26) Viney, C.; Yoon, D. Y.; Reck, B.; Ringsdorf, K. *Macromolecules* **1989**, *22*, 4088.

Registry No. DMAc, 127-19-5; PBA (homopolymer), 25136-77-0; PBA (SRU), 24991-08-0; PABH-T (copolymer), 27102-68-7; (PABH)(TC)($H_2NC_6H_4$-*p*-CO_2H) (block copolymer), 136537-20-7; LiCl, 7447-41-8.