Synthesis of block copolymers based on poly(*p*-benzamide) with a polyamide benzimidazole

Giuseppina Conio* **and Aldo Tealdi**
Centro di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali, CNR, Via De Marini 6, 16149 Genova, Italy

and Enrico Marsano
Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, 16132 Genova, Italy

and Alberto Mariani
Dipartimento di Chimica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

and Igor Ponomarev
Institute of Organo-Element Compounds, Academy of Sciences of Russia, Vavilov Str. 28, 117813, GSP-1, Moscow, Russia

(Received 28 July 1993)

A diblock copolymer based on poly(*p*-benzamide) (PBA) and poly(2-phenylene-(5-benzimidazole))isophthalamide (PABI) was synthesized by direct coupling reaction between acylchloride and amino end groups of the two homopolymers. Soxhlet extraction with *N*,*N*′-dimethylacetamide completely removed unreacted PABI and allowed determination of copolymer content and composition of the unextracted fraction (by u.v. data and viscosity measurements). Preliminary results on phase behaviour are given and analysed in terms of block length.

(Keywords: coupling reaction; block copolymers; phase behaviour)

Introduction

In a previous paper[1] a new procedure to obtain diblock copolymers based on poly(*p*-benzamide) (PBA) and poly(terephthalamide of *p*-aminobenzhydrazide) (PABH-T) was described. The coupling reaction between the acylchloride terminal group of PABH-T and the amino end group of PBA enabled copolymer formation. Whilst it was easy to remove unreacted PABH-T from the reaction mixture, no selective solvent was found suitable for the separation of the copolymer and the unreacted PBA.

The phase diagram of the above block copolymer in *N*,*N*′-dimethylacetamide (DMAc) + 3% LiCl was determined and compared[2] with the behaviour predicted by the Matheson–Flory theory[3]. The good agreement found prompted us to synthesize another copolymer, changing the nature of the semirigid block. Our attention was focused on polyamide benzimidazoles, a class of aromatic polymers recently synthesized in Russia[4] and characterized by a persistence length[5] of ~85 Å. This value should enable the formation of an anisotropic phase at polymer concentrations higher than ~35%. However, this behaviour was not experimentally observed, analogously to PABH-T[6]. In this preliminary paper, we report our data on the synthesis and the phase diagram of a block copolymer based on PBA and poly(2-phenylene-(5-benzimidazole))isophthalamide (PABI). Optimization of reaction conditions and the complete characterization of the copolymers synthesized are in progress and will be reported elsewhere.

Experimental

Materials and methods. Isophthaloyl chloride (ICl) (Fluka–Buchs) was recrystallized from boiling n-hexane prior to use. 5(6)-Amino-2(*p*-aminophenyl)benzimidazole (DAB) (synthesized by one of us (I.P.) in Moscow) was vacuum dried for 12 h at 100°C and stored over P_2O_5. Ethyldiisopropylamine (EDPA) (Merk–Schuchardt) was stored over Riedel type 4A molecular sieves. DMAc (Fluka–Buchs) was vacuum distilled over CaH_2 and stored over Riedel type 4A molecular sieves. Lithium chloride (Riedel-de Haen, RG) was vacuum dried for 24 h at 200°C.

The PBA sample, analogous to that used in a previous investigation[7], was synthesized following the method of Yamazaki *et al.*[8]. Its intrinsic viscosity, $[\eta]$, in 96% H_2SO_4 at 25°C was $1.50\,\mathrm{dl\,g^{-1}}$, corresponding to a viscosity average molecular weight of 11 400 in terms of the relationship given by Schaefgen *et al.*[9]. The M_n value was evaluated assuming that $M_w/M_n \approx 1.6$, as previously determined[7].

Solution viscosity and u.v. spectral measurements on homo- and copolymers were performed according to methods already utilized[2]. Critical concentration for the appearance of mesophases (C_p') was determined by polarized optical microscopy[2].

Procedure. PABI was synthesized in the first step. To a 100 ml three-necked round-bottom flask fitted with a mechanical stirrer and an inlet and outlet for argon were added 30 ml of DMAc, 1 g of LiCl and 0.006 mol (1.346 g) of DAB.

---

* To whom correspondence should be addressed

0032-3861/94/05/1115-03

The mixture was stirred at room temperature and, after dissolution, cooled to −15°C with an external ice/salt bath; 0.006 mol (1.220 g) of ICl were added slowly with stirring. Overall reaction time was 1.5 h at −15°C plus 1 h at room temperature.

After cooling at −15°C, a 5% solution of PBA in DMAc + 3% LiCl was added slowly, in about 1 h, to the mixture followed by 12 h at room temperature and 2 h at 50°C with stirring in argon atmosphere. A small amount of EDPA was introduced into the reaction vessel at the beginning. The reaction mixture was poured into distilled water and washed several times. Finally, the precipitated material was extracted with methanol in Soxhlet apparatus and stirred twice with DMAc at 70°C to remove completely the unreacted PABI.

Polymer recovery and characterization. Extracted PABI in DMAc solution was poured into water in order to characterize the unreacted homopolymer. The unsolubilized fraction (termed PBA-DC) was composed of unreacted PBA and diblock copolymer. The recovered PABI and the remaining fraction were characterized by u.v. and viscometry. U.v. spectral measurements in DMAc + 3% LiCl to determine the copolymer composition, were performed at wavelengths of 346 and 370 nm. Calibration was based on mechanical mixtures of the two homopolymers, assuming absorbance additivity rules as previously adopted[2].

Under the same conditions, a PABI sample was synthesized for use in M_w evaluation by sedimentation[10]. The partial specific volume of PABI in DMAc + 3% LiCl was determined by pycnometry at 25°C and found to be 0.669 ml g^{-1}. The density of the solvent was 0.963 g ml^{-1}. The M_w, calculated as described above, was equal to 54 000 (ref. 10).

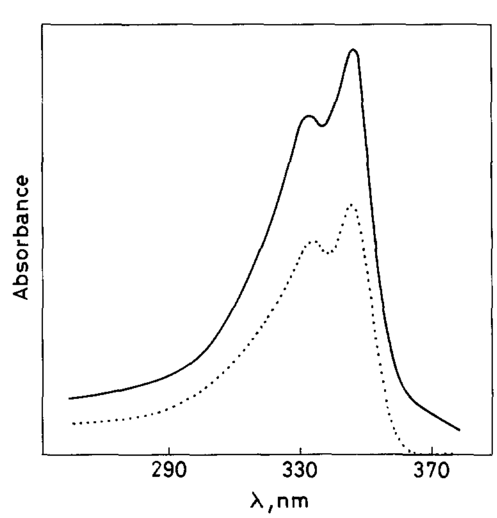

Figure 1 U.v. absorption spectra of PBA (····) and PBA-DC (——) in DMAc + 3% LiCl

Table 1 Characterization data of PBA, PABI and PBA-DC

Sample	$[\eta]$[a] (dl g^{-1})	$[\eta]$[b] (dl g^{-1})	M_w	M_n	C_p' (%, w/w)
PBA	1.50	1.84	11 400	7 100	6
PABI	1.37	1.32	54 000	32 000	n.d.[c]
PBA-DC	1.93	–	–	–	

[a] Measured in H_2SO_4 96% at 25°C
[b] Measured in DMAc + 3% LiCl at 21°C
[c] Not determined

Results and discussion

The characterization data of both PBA and PABI homopolymers, and the PBA-DC are reported in *Table 1*.

The intrinsic viscosities of the PABI whole sample, as-synthesized, and the fraction extracted by DMAc, were the same.

The M_w values were calculated using the Schaefgen relationship[9] for PBA and determined from sedimentation velocity measurements for PABI, as reported elsewhere[10]; the values are 11 400 and 54 000, respectively, and the corresponding M_n values are ~7100 and 32 000. They were determined assuming that $M_w/M_n \approx 1.6$ for PBA[6] and ≈ 1.7 for PABI[5].

The PBA-DC sample, a mixture of unreacted PBA and the copolymer, has an intrinsic viscosity of 1.93 dl g^{-1}, a value higher than those of the two homopolymers. This increase of $[\eta]$ can only be attributed to relevant copolymer formation. Indeed, the same $[\eta]$ value for both the PABI whole sample and the extracted fraction rules out any spurious contribution due to high molecular weight enrichment of unextracted PABI. The percentage increase of $[\eta]$ is ~30%, a value almost identical to that found for the system PBA/PABH-T[1]. Similarly, for the present system we may assume this increase as evidence for block copolymer formation. A further indication in favour of this attribution is obtained from the u.v. spectra. *Figure 1* shows the u.v. spectra of PBA-DC and PBA; applying absorbance additivity rules, we can obtain an overall PABI content of ~27% (w/w) in the PBA-DC sample, equivalent to ~33% (w/w) as copolymer, assuming a two-block structure.

In the present work we also report preliminary data on the phase behaviour of PBA/copolymer solutions in DMAc + 3% LiCl. The experimental results are reported in *Table 2*.

Only a very small fraction of copolymer is present in the anisotropic phase, as evidenced by u.v. analysis. This behaviour is apparently in disagreement with the results

Table 2 Summary of data related to the phase behaviour of the PBA-DC/DMAc + 3% LiCl system

Bulk solution			Isotropic phase			Anisotropic phase		
Cp[a] % (w/w)	PABI % (w/w)	Cop[b] % (w/w)	Cp[a] % (w/w)	PABI % (w/w)	Cop[b] % (w/w)	Cp[a] % (w/w)	PABI % (w/w)	Cop[b] % (w/w)
8.57	27	33	7.46	46.6	57	10.66	1.5	2.0
9.20	27	33	8.10	51.0	62	11.4	2.0	2.5

[a] Polymer concentration
[b] Copolymer concentration

obtained for the block copolymer of PBA/PABH-T[1,2], which is present to a significant degree in the anisotropic phase (~19%). A possible explanation is linked to the large differences in the length of the PABH-T and PABI blocks.

Indeed, the M_w of our PABI sample is very high (~54 000); the low content of copolymer in the anisotropic phase is probably due to the extreme length of the PABI block. Consequently, the synthesis of block copolymers with shorter PABI sequences is in progress and will be reported elsewhere, together with a full description of phase behaviour of both block copolymers and homopolymer mechanical mixtures.

Acknowledgement

This research was supported by CNR, the Italian Research Council, through 'Chimica Fine e Secondaria II' project and 40% MURST.

References

1 Marsano, E., Bianchi, E., Conio, G., Mariani, A. and Russo, S. *Polym. Commun.* 1991, **32**, 45

2 Conio, G., Marsano, E., Bonfiglioli, F., Tealdi, A., Russo, S. and Bianchi, E. *Macromolecules* 1991, **24**, 6578

3 Matheson, R. R. Jr and Flory, P. J. *Macromolecules* 1981, **14**, 954

4 Serkov, A. T., Glazunov, V. B., Komissarov, V. I., Serkova, L. A., Kulakov, V. N., Nikiforov, I. M., Toloknov, R. Ye., Sokolovskii, B. M. and Rassolov, O. P. USSR Patent 664972, 1979

5 Pavlov, G. M., Selyunin, S. G., Shil'dyayeva, N. A., Yakopson, S. M., Efros, L. S. and Usova, S. V. *Polym. Sci. USSR* 1985, **8**, 1823

6 Bianchi, E., Ciferri, A., Preston, J. and Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 863

7 Conio, G., Tealdi, A., Russo, S. and Bianchi, E. *Polymer* 1990, **31**, 362

8 Yamazaki, N., Matsumoto, M. and Higashi, F. *J. Polym. Sci., Polym. Chem. Edn* 1975, **13**, 1373

9 Schaefgen, J. R., Foldi, V. S., Logullo, F. M., Good, V. H., Gulrich, L. W. and Killian, K. L. *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.* 1976, **17**, 69

10 Timofejeva, G. I. unpublished results, 1992