Polymer Bulletin 37, 345–351 (1996)

Polymer Bulletin

Block copolymers

I. Poly(*p*-benzamide)-*b*-poly(propylene oxide)*

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Received: 2 December 1995/Revised version: 2 May 1996/Accepted: 3 May 1996

SUMMARY

The preparation of acid chloride of poly(propylene oxide), PPO, the synthesis of prepolymer poly(p-benzamide), and of block copolymers of poly(p-benzamide)-b-poly(propylene oxide) are reported. The preparation of prepolymer poly(p-benzamide), PBA, and activated PPO, as well as PBA-PPO block copolymer are discussed according to their FTIR spectra.

INTRODUCTION

Aromatic polyamides, specially poly(p-benzamide) and poly(p-phenylene terephthalamide), are high modulus and high temperature resistant polymers. Extremely resistant polymers are good in one sense but inadequate in other, i.e., they require special fabrication processes because conventional processing techniques cannot be used. One way to prevent this situation may be by the use of block copolymers in which one rigid highly resistant segment is combined with a flexible one [1-4].

The present paper describes the preparation of activated poly(propylene oxide), PPO, and its coupling with poly(p-benzamide), PBA, to obtain a block copolymer that combines a rigid and a flexible segment.

EXPERIMENTAL

Reagents

N-Methyl pyrrolidone, NMP, (Aldrich), pyridine, Py, (Aldrich), triphenylphosphite, TPP (Aldrich) were distilled under reduced pressure. p-Aminobenzoic acid, p-ABA, (Aldrich) was dried under vacuum at 110°C while lithium chloride was dried at 325°C during 12 hours.

Terephthaloyl chloride TCl, was prepared by direct chlorination of terephthalic acid using phosphorous pentachloride [5], and purified by sublimation under dry nitrogen atmosphere. The resulting product was characterized by FTIR analysis.

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* Presented in part at Segundo Simposio Chileno de Química y Físico-Química de Polímeros, CHIPOL II. Quilpué, Chile. November 30–December 2, 1994

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Synthesis of poly(p-benzamide).

PBA was prepared according to Yamazaki et al. [1]. The reaction was performed in a three neck conical-shaped reactor, equipped with a mechanical stirrer. The equipment was thoroughly flamed under a current of dry nitrogen gas. Afterwards, and still under dry N_2-atmosphere, were charged by syringe 82.08 g (0.828 mol) of NMP and 58.68 g (0.742 mol) of Py. Then 5.92 g (0.140 mol) of LiCl and 11.48 g (0.084 mol) of p-aminobenzoic acid were added. The mixture was warmed to 100°C with continuous stirring till complete dissolution. To the clear solution were added 26.05 g (0.084 mol) of TPP. The reaction mixture was maintained with agitation for nearly 90 minutes. The resulting paste was dispersed in methanol, chipped in a blender and extracted with methanol in a Soxhlet extractor for four hours and dried in vacuo. Finally, 9.42 g PBA with an inherent viscosity of 1.54 dL/g, (concn., 0.504 %) in 98% sulfuric acid at 25°C, were obtained.

Activation of poly(propylene oxide).

The acid chloride derivative of PPO was prepared by direct reaction of low molecular weight PPO (Aldrich, MW = 4000) with TCl through a procedure slightly different from that used by Zdrahala et al. when preparing the acid chloride derivative of poly(ethylene oxide)[6]. TCl (0.83 g) were placed in a 100 mL flask equipped with a magnetic stirrer and warmed to 83-85°C. To the molten TCl were added slowly, drop by drop, 4.7 g of poly(propylene oxide). The reaction mixture was stirred for 20 minutes after PPO addition and then the excess of TCl was removed by sublimation. A highly viscous transparent clear liquid was obtained.

Coupling between PBA and PPO.

The coupling between PBA and PPO was accomplished by direct reaction between activated PPO and PBA prepolymers.

In a three-neck flask with a stirrer and cooled to -22°C under a current of dry nitrogen gas were placed, in large excess, 1.004 g (0.241 mmol) of activated PPO, to which, under vigorous stirring and dry nitrogen atmosphere were added drop by drop, during one hour, 20 mL (1.75×10^{-2} mmol PBA) of 1% PBA solution in DMAc (at 3% LiCl). After PBA addition, the temperature was increased slowly to -5°C in about 15 hours with continuous stirring and under N_2-atmosphere. Afterwards the mixture was precipitated into cold methanol, the product was washed twice with water, twice with methanol, and extracted for 10 hours with methanol in a Soxhlet extractor, to eliminate remaining PPO. Finally, the copolymer was dried under vacuum at 60°C.

RESULTS AND DISCUSSION

The rigid PBA block was obtained through polycondensation of p-aminobenzoic acid. The resulting polymer with an inherent viscosity of 1.54 dL/g (MW 11000 to 12000) was insoluble in usual solvents. For coupling PBA was dissolved in DMAc containing 3% LiCl.

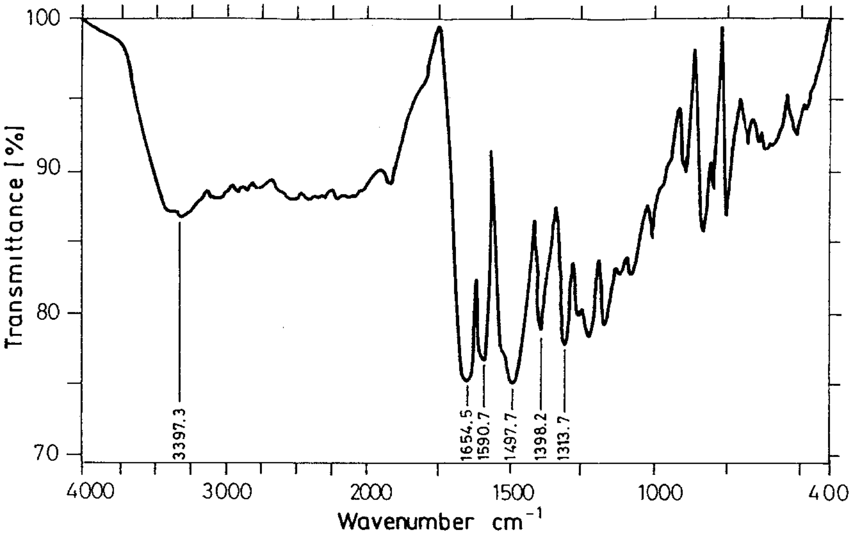

Figure 1. FTIR spectrum of PBA.

Figure 1, shows the FTIR spectrum of the PBA prepared. The spectrum clearly differentiates the monomer p-aminobenzoic acid from PBA. The pertinent signals of spectrum are summarized in Table 1.

Table 1. FTIR absorptions of PBA.

Signal, cm^{-1}	Functional group
3397.3	amide N-H
1654.5	amide C=O
1590.7 and 1497.7	aromatic C=C
1590.7 and 1398.2	carboxylate O-C=O
1313.7	amide C-N

Figure 2 shows the FTIR spectra of PPO (Fig. 2a) and of activated PPO (Fig. 2b). The signal at 3469.6 cm^{-1}, which corresponds to O-H stretching of terminal hydroxyl groups (Fig. 2a), is not present in act-PPO (Fig. 2b). The (2b) spectrum shows signals at 1723.7 cm^{-1} (C-O, carbonyl, ester stretching) and 1779.6 cm^{-1} (C-O carbonyl, COCl stretching, terminal group of act-PPO) and at 699.2 cm^{-1} (C-Cl stretching) confirming that activation reaction has occurred.

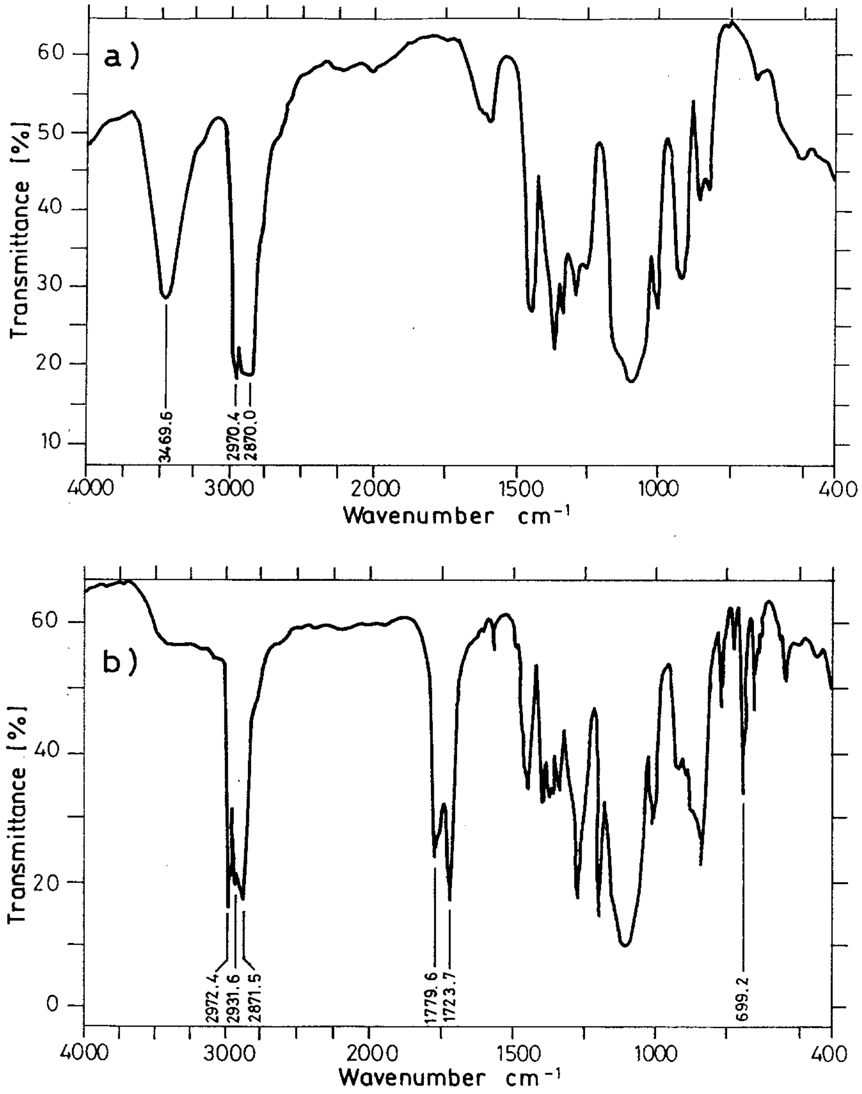

Figure 2. FTIR spectra of (a) PPO; and (b) activated poly(propylene oxide), act-PPO.

Figure 3, shows the FTIR spectrum of the PBA-PPO block copolymer resulting of PBA and act-PPO. The spectrum shows signals belonging to both blocks. These signals are summarized in Table 2.

Table 2. FTIR absorptions of PBA-b-PPO.

Signal, cm^{-1}	Functional group	Prepolymer patterns
3345.4	amide N-H	3328 PBA
2970.7, 2932.9, and 2869	aliphatic C-H	2972, 2931, 2871 act-PPO
1790.7	anhydride C=O	none
1724.2	ester C=O	1723.7 act-PPO
1658.8	amide C=O	1656.4 PBA
1602.1	aromatic C=C	1588 PBA; 1575 act-PPO
1502.6	aromatic C=C	1493 PBA; 1498 act-PPO
1406.8 and 1373.8	aliphatic CH_3	1405 and 1379 act-PPO
1316.5	aromatic amide N-H	1312.2 PBA
1232.5	ester O-C=O	1229 PBA
1182	aromatic C-H	1177 PBA; 1197 act-PPO
1068	ether C-O-C	1108 act-PPO

In the overtone region there is a very good agreement between the absorptions shown by the PBA-PPO and the corresponding PBA and PPO prepolymers.

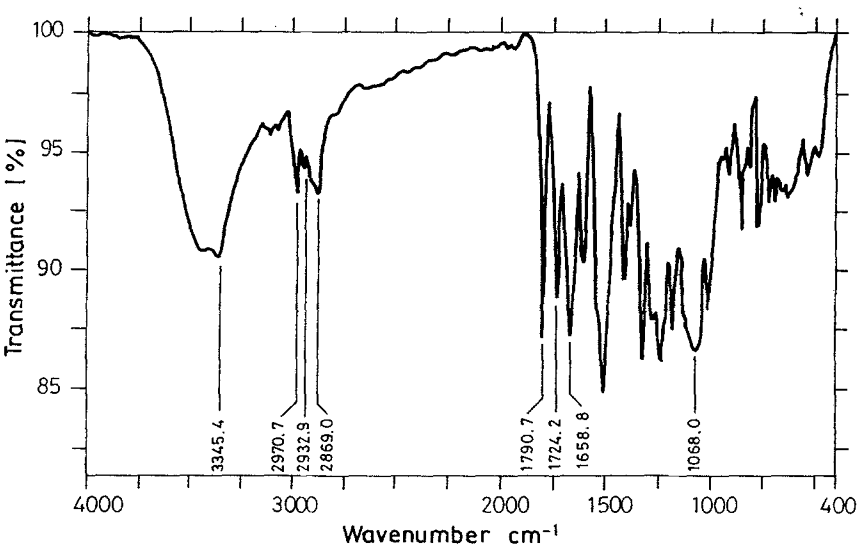

Figure 3. FTIR spectrum of block copolymer PBA-PPO.

CONCLUSIONS

The FTIR spectra of PBA and act-PPO, as well as of the block PBA-PPO agrees with their expected chemical structures and indicate the presence of both blocks in the copolymer.

1. The most relevant signals are:
   i) 1779.6 cm^{-1} and 1723.7 cm^{-1} (Fig. 2b) corresponding, respectively, to COCl terminal and to CO ester linkage of act-PPO.
   ii) 1790.7 cm^{-1} (Fig. 3) corresponding to anhydride group resulting from carboxylic end of PBA and halide carbonyl group of TCl end of act-PPO.

2. The observed shift of signal to more energized region compared with signal of similar groups in prepolymers, are in agreement with the lower flexibility of groups resulting from their incorporation to the copolymer.

ACKNOWLEDGEMENTS

This work has been carried out with the financial support from Commission of European Communities, Contract N° CI1*-CT93-0322, from Departamento de Investigaciones Científicas y Tecnológicas, Universidad de Santiago de Chile (DICYT-USACH), Grant 9232-RC, and from Dirección de Investigación, Universidad de Concepción. Authors gratefully acknowledge Dr. J. Preston from Research Triangle Institute for his skillful help in PBA preparation.

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