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Block copolymerization of *N*-phenylmaleimide onto poly(styrene) and poly(butadiene): synthesis and characterization

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SUMMARY

Synthesis and characterization of novel block copolymers of N-phenylmaleimide (N-PMI) and styrene or butadiene are described. Block copolymerization of N-PMI to polystyrene or polybutadiene prepolymers was evidenced by GPC, ^{1}H NMR, and thin layer chromatographic analyses of the products.

INTRODUCTION

Block copolymerization is a promising method for preparation of polymeric material with new properties, which are hardly obtained from random copolymerization of the corresponding monomers. Anionic polymerization is a useful tool for block copolymerization and actually applied in an industrial field as a method for synthesis of styrene/butadiene block copolymer.

Recently, anionic polymerization of N-phenylmaleimide (N-PMI) has been intensively studied. It has been revealed that N-PMI is easily polymerized by basic species as initiators[1-3]. The polymerization proceeds with living character –no termination and no chain transfer reactions[3,4]. Utilizing this nature, block copolymer with controlled chain length of poly(N-PMI) can be prepared. Poly(N-PMI) shows high thermostability and strong solvent resistance though it is brittle and thus difficult to be thermoprocessed.

This article is concerned with preparation of N-PMI/styrene and N-PMI/butadiene block copolymers. Poly(styrene) is a typical thermoplastic polymer which is easily processed. Block copolymerization of N-PMI with styrene can be expected to afford polymers that would excel poly(N-PMI) in processability and polystyrene in thermostability. Block copolymerization of N-PMI with butadiene can produce novel elastomers different from butadiene homopolymer in thermostability and solvent resistance.

EXPERIMENTAL

All experiments related to polymerization were carried out under a purified nitrogen atmosphere in order to exclude oxygen and moisture.

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Reagents: N-PMI was purified as previously described[1]. THF and toluene (Tol.) were purified by the usual methods. Commercial *sec*-butyllithium was used after determination of the concentration of active species. styrene was dried by refluxing over calcium hydride and distilled under reduced pressure of nitrogen atmosphere. Butadiene was dried by passing through a molecular sieves 4A column followed by refluxing over calcium hydride, and purified by distillation of a trap-to-trap method before use.

Block copolymerization of N-PMI: To a solution of living polystyrene or polybutadiene which prepared by the anionic polymerization method under a nitrogen atmosphere, a solution of N-PMI was added. The reaction was stopped with addition of methanol/hydrochloric acid.

Isolation of block copolymers: The reaction mixture was poured into a large amount of precipitant (methanol for styrene/N-PMI block copolymer, hexane for butadiene/N-PMI block copolymer). The precipitate was collected by filtration, washed several times with the precipitant, and dried. The precipitate was subjected to Soxlet extraction with ether. Residue containing block copolymer was subjected to Soxlet extraction again with benzene. After almost whole amount of benzene was removed from the extract, the block copolymer was isolated by freeze drying. Fig. 1 shows a flow chart for these experiments.

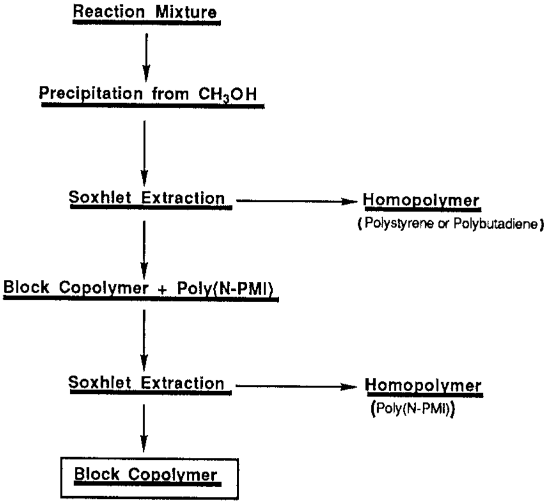

Fig. 1. Flow chart for isolation of block copolymers

Measurements: ^{1}H NMR spectra were recorded on a JEOL GSX-270 FT-NMR spectrometer. Gel permeation chromatogram was obtained with a TOSOH HLC-820A apparatus at 38°C with a series of TSK gel columns (G4000HXL-G3000HXL-G2000HXL) using THF as eluent (flow rate 1.0 ml/min). Thin layer chromatography (TLC) was carried out on a Silica gel plate (Kieselgel 60 F_{254} from Merck).

RESULTS AND DISCUSSION

Block copolymerization of N-PMI

Results of block copolymerization of N-PMI to polystyrene or polybutadiene are shown in Table I. Living polystyrene prepolymers can be prepared in both polymerization systems initiated with *sec*-butyllithium in THF or toluene, though a very small amount of living species might be inactivated. Block copolymerization takes place by the addition of a N-PMI solution to the living system. In the method employed in this study, narrower molecular weight distribution is observed for both prepolymer and block copolymer when using toluene instead of THF as a polymerization solvent while it takes much longer polymerization time compared to the homopolymerization of N-PMI under similar conditions.[2]

Living polybutadiene can be also prepared in the polymerization systems initiated with *sec*-butyllithium in THF or toluene as a solvent. Molecular weights of

Table 1. Block Copolymerization of N-PMI onto polystyrene and polybutadiene with *sec*-Butyllithium[a]

Run	Init. charged (mmol)	Solv.	Preparation of prepolymer					Block copolymeriz of N-PMI				Mol ratio in block copolymer (monomer unit of of prepolymer/ N-PMI unit)[d]
			Monomer[b]	Temp. (°C)	Time (h)	Conv. (%)	M_{GPC}[c] $\times 10^{-3}$	N-PMI (mmol)	Temp. (°C)	Time (h)	Conv. (%)	
1	0.2	THF	ST[e]	-78	0.25	98	5.0	5	0	3	11	18.1
2	0.4	Tol.	ST[e]	0	48	97	3.1	5	0	48	45	4.3
3	1.0	THF	BD[f]	0	6	85	1.1	10	0	24	36	2.4
4	1.0	Tol.	BD[f]	22	6	73	1.1	10	22	24	67	1.1

a. Total volume of the polymerization system: 10 ml for preparation of prepolymer, 25 ml for block copolymerization.
b. Monomer charged, 10 mmol.
c. Peak molecular weight calibrated by poly(styrene) standard samples.
d. Determined by ^1H NMR.
e. Styrene.
f. Butadiene

polybutadiene suggest that some amount of the living species is inactivated for each system. Block copolymerization of N-PMI to the living prepolymer can be, however, initiated by the addition of a N-PMI solution to the polymerization system of butadiene after removal of unchanged butadiene. Higher temperature is favorable for N-PMI block polymerization.

Characterization of block copolymer

Fig. 2 shows GPC chromatograms of the block copolymer (**A**) and polystyrene as a prepolymer (**B**). An increase in polymer molecular weight owing to block copolymerization is observed. Fig. 3 depicts the ^{1}H NMR spectrum of styrene/N-PMI block copolymer. Signals of the phenyl protons of both styrene and N-PMI units are observed at 6.0-7.5 ppm. A broad peak around 4 ppm is assigned to the methine protons in the main chain of poly(N-PMI)[3], and signals at 0.7-2.2 ppm are assignable to the methylene and methine protons of styrene units[5]. Fig. 4 illustrates TLC patterns of styrene/N-PMI block copolymer, styrene homopolymer and N-PMI homopolymer. The block copolymer gave spots (**a** in (**A**) and (**B**)) well separated from those of both homopolymers (**b** in (**A**) and **c** in (**B**)). From these results, it is concluded that a new type block copolymer of styrene and N-PMI is synthesized.

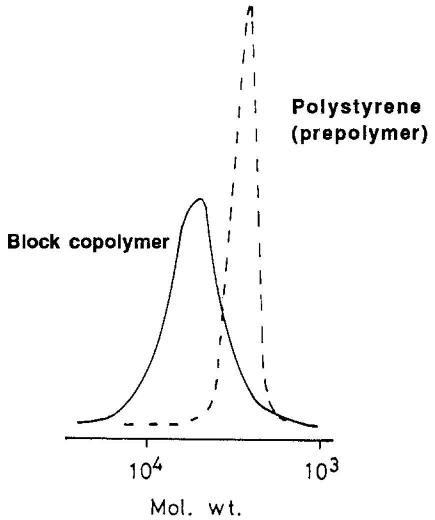

Fig. 2. GPC chromatograms of styrene/N-PMI block copolymer (**A**), and polystyrene prepolymer (**B**) (Run 2 in Table 1).

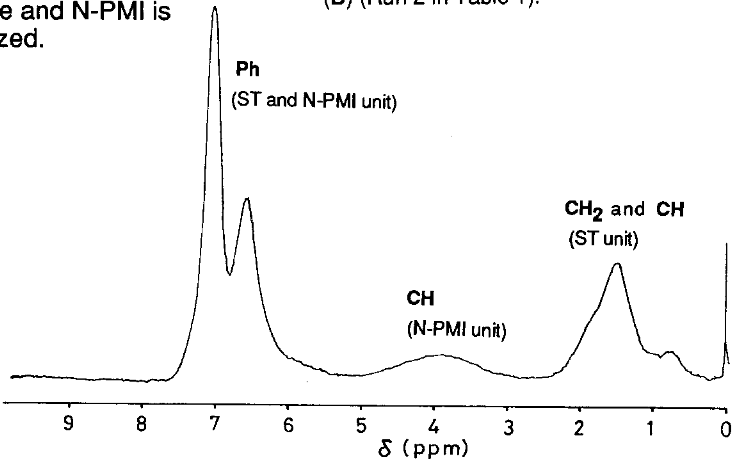

Fig. 3. ^{1}H NMR of styrene/N-PMI block copolymer.

Fig. 5 shows GPC chromatograms of block copolymer (**A**) and polybutadiene obtained with *sec*-butyllithium in toluene at 22°C (**B**). Increase of the molecular weight are observed for block copolymer compared to the prepolymer. ^{1}H NMR spectrum of poly(styrene-*b*-N-PMI) are shown in Fig. 6. The signals observed at 1-2 ppm are assignable to the protons in the polybutadiene[6]. The signals observed at 7.5 and 4 ppm (broad) are assigned to the phenyl and methine protons, respectively, in poly(N-PMI)[3]. Fig. 7 depicts TLC patterns of butadiene/N-PMI block copolymer, butadiene and N-PMI homopolymers. Spots of the block copolymers (**a** in (**A**) and (**B**)) are different from those of homopolymers (**b** in (**A**) and **c** in (**B**)). These results indicate that the novel block copolymers containing polybutadiene as soft segment and poly(N-PMI) as hard segment are synthesized.

Thin films can be prepared by casting on clean glass surface from dichloromethane solutions of poly(butadiene-*b*-N-PMI) while N-PMI homopolymer did not afford a film.

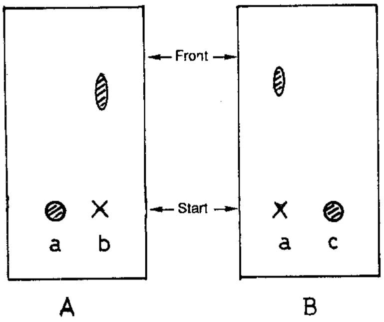

Fig. 4. TLC patterns of styrene/N-PMI block copolymer (**a**), polystyrene (**b**), and poly(N-PMI) (**c**). Developed with hexane/ethyl acetate=2/1 (v/v) for plate **A**, and hexane/ethyl acetate 1/2 (v/v) for plate **B**.

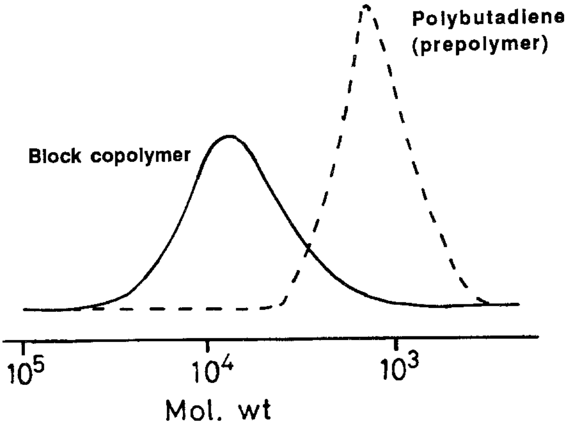

Fig. 5. GPC chromatograms of butadiene/N-PMI block copolymer (**A**), and polybutadiene prepolymer (**B**) (Run 4 in Table 1).

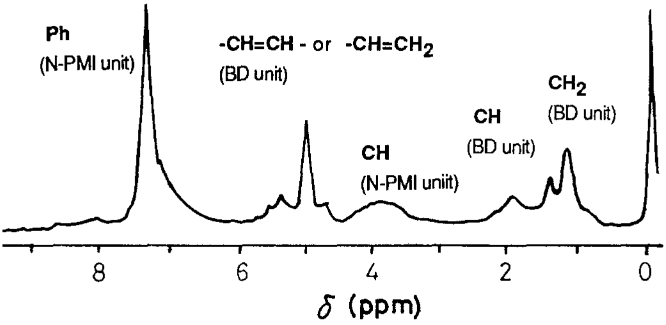

Fig. 6. ^{1}H NMR of butadiene/N-PMI block copolymer.

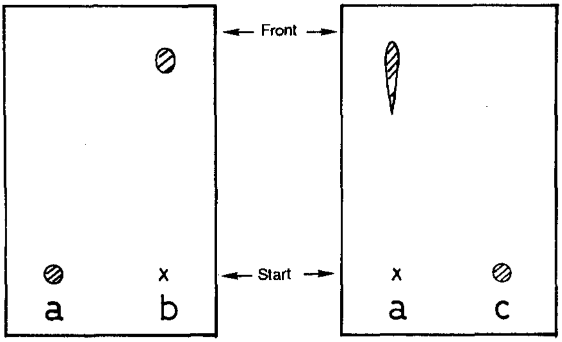

Fig. 7. TLC patterns of butadiene/N-PMI block copolymer (**a**), polybutadiene (**b**), and poly(N-PMI) (**c**). Developed with hexane/chloroform=1/2(v/v) for plate **A**, and ethyl acetate 1/2 (v/v) for plate **B**.

REFERENCES

1. R. C. P. Cubbon, Polymer. 6, 419 (1965).
2. T. Hagiwara, J. Mizota, H. Hamana, T. Narita, Makromol.Chem., Rapid Commun., 6, 169 (1985).
3. T.Hagiwara,T.Shimizu,T.Someno,T.Yamagishi,H.Hamana,T.Narita, Macromolecules, 21, 3324 (1988).
4. T. Hagiwara, T. Shimizu, T. Uda, H. Hamana, T. Narita, J. Polym. Sci., Polym. Chem. Ed., 28, 185 (1990).
5. F. A. Bovey, G. V. D. Tiers, G. Filipovich, J. Polym. Sci., 38, 73 (1959).
6. Y. Tanaka, Y. Takeuchi, M. Kobayashi, H. Tadokoro, J. Polym. Sci., A2 9, 43 (1971).

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