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Novel block copolymers containing poly(phenylmaleimide) segments: Block copolymerization of *N*-phenylmaleimide onto poly(oxyethylene) and poly(butadiene)

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Summary

Novel block copolymers having poly(N-phenylmaleimide) segments onto poly(oxyethylene) or poly(butadiene) were synthesized. The block copolymerization of N-phenylmaleimide was carried out anionically with lithium alkoxides of poly(ethylene glycol) or α,ω-dihydroxypoly(butadiene). The block copolymers obtained were characterized by ^{1}H NMR, GPC and TLC.

Introduction

N-Phenylmaleimide (N-PMI) is easily polymerized with alkali metal alkoxides such as lithium *tert*-butoxide and potassium *tert*-butoxide to yield poly(N-PMI)[1-3]. This anionic polymerization proceeds with living character so that the chain length of the polymer obtained can be predictable from the conversion of N-PMI[2]. Utilizing these characteristics, various kinds of block copolymers can be produced with macromolecules possessing hydroxyl groups as terminal groups since the alkali metal alkoxides of these polymers can be prepared with facility by the reaction between hydroxyl groups and alkali metal or organometallic compounds. The macromolecular compounds with hydroxyl groups at one or both ends are able to be conventionally synthesized from several methods such as anionic polymerization followed by the treatment of ethylene oxide and hydrolysis[4].

In this paper, the preparation and characterization of novel block copolymers by the anionic block copolymerization of N-PMI onto poly(oxyethylene) (POE) and poly(butadiene) (PBD) are described.

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Experimental

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

Reagents

N-PMI, toluene and THF were purified in the same way as described in a previous paper[2]. Benzene and hexane were purified and dried by the same way as that of toluene. Poly(ethylene glycol) (PEG: from Wako Pure Chemical Industries, LTD.; average mol. wt.= 1000 (PEG_{1000}) or 1540 (PEG_{1540})), α,ω-dihydroxypoly(butadiene) (HPB: from Japan Synthetic Rubber Co., LTD.; average mol. wt.=3100) were dried as follows: ca. 1g of PEG or HPB were dissolved into ca. 100 ml of benzene. Most of benzene was distilled off in order to remove a trace amount of water as benzene azeotrope. Finally a trace amount of benzene remained was removed under vacuum. Butyllithium (hexane solution) was used after determination of the concentration.

Block Copolymerization

Preparation of Macromolecular Alkoxide Initiators:

To the benzene solution of prepolymer(PEG or HPB), an excess amount (1.5 times equivalent of hydroxyl group in prepolymer) of butyllithium (hexane solution) was added and stirred for 6 h at 40°C. After benzene was removed by freeze drying the residue was washed more than four times with hexane. The THF or toluene solution of lithium alkoxide of the prepolymer was used for block copolymerization after determination of the concentration of alkoxy groups by means of titration.

Block Copolymerization of N-PMI onto Prepolymer:

To the solution of alkoxide of the prepolymer, the solution of N-PMI was added with stirring under nitrogen atmosphere. The color of the reaction mixture turned red and persisted until the reaction was stopped with addition of methanol/hydrochloric acid mixture after the definite reaction time.

Isolation of Block Copolymers

POE/Poly(N-PMI) Block Copolymer:

The reaction mixture was poured into a large amount of methanol. Precipitate was collected by filtration, washed several times with methanol and dried. The precipitate was dissolved into THF and poured into benzene. The precipitate, if formed, was filtered off and the filtrate containing block copolymer was subjected to evaporation. After almost whole

amount of the solvent was removed the residue was dissolved again into a small amount of benzene. The block copolymer was then isolated by freeze drying.

PBD/Poly(N-PMI) Block Copolymer:

Block copolymer was isolated by the same way as that for POE/poly(N-PMI) copolymer except using hexane instead of methanol as the first precipitant.

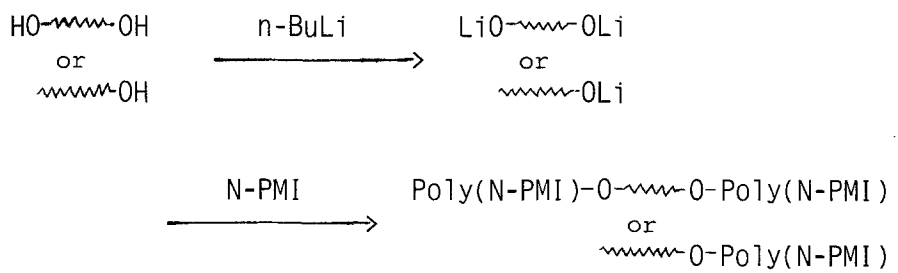
Measurement

^{1}H-NMR spectra were recorded on a HITACH R-600 FT-NMR spectrometer using deuterated chloroform as solvent at 35°C. GPC was measured with column series of TSK gel G4000HXL-G3000HXL-G2000HXL (TOSOH Co., Tokyo) using THF as eluent. The exclusion limits of molecular weight: $4x10^5$ for G4000HXL, $6x10^4$ for G3000HXL $1x10^4$ for G2000HXL. TLC was performed on a Merck silica 60 silica gel plate.

Results and discussion

Synthesis of block copolymer

The scheme of the block copolymerization assumed here is as follows:



The results of block copolymerization are summarized in Tab. 1. Regardless of chemical structures and molecular weights of the prepolymers, block copolymerization of N-PMI takes place on the prepolymers and less than 10% of prepolymers are remained unchanged. Especially, in the case of HPB as a prepolymer the amount of the non-blocked prepolymer is negligibly small. Presence of non-blocked prepolymers is presumably attributed to incomplete conversion of hydroxyl groups into lithium alkoxides in the prepolymers or deactivation of the alkoxide groups such as hydrolysis.

Tab. 1 Block Copolymerization of N-PMI onto POE and PBD[a)]

Run	Prepolymer	-OH group in prepolymer (mmol)	N-PMI (mmol)	Non-blocked prepolymer (%)	N-PMI block copolymd.[b)] (%)
1	PEG_{1540}[c)]	0.12	12	7	55
2	PEG_{1540}[c)]	0.29	12	8	76
3	PEG_{1000}[d)]	0.10	10	4	68
4	PEG_{1000}[d)]	0.10	1.0	6	89
5	HPB[e)]	0.77	4.0	0	73

a) Polymerization condition: temp. 0°C; time, 24h; in THF. b)Determined by ^1H NMR. c)Poly(ethylene glycol): Mn=1540. d) Poly(ethylene glycol): Mn=1000. e) Poly(butadiene) with hydroxyl groups at both ends: Mn=3100.

Characterization of Block Copolymers

As shown in the GPC eluograms (Fig. 1), both block copolymers elute at the range of higher molecular weight (solid line) compared with those of the prepolymers (dotted line). The unimodal molecular weight distributions of the prepolymers are maintained for the block copolymers. TLC measurements for block copolymers showed that each block copolymer developed in the different position from the corresponding prepolymer and from homopolymer of poly(N-PMI). It was, therefore, evidenced that the block copolymer obtained here was not the mixture of the prepolymer and poly(N-PMI). The results of TLC measurements support the conclusion derived from the GPC eluograms.

Fig. 2 shows ^1H-NMR spectra of the block copolymers from PEG (**A**) and HPB (**B**) as prepolymers. In each spectrum the signals which are assignable to the segments of the prepolymers (3.6 ppm, CH_2 for POE; 1.8 ppm, CH_2 and 5.4 ppm CH= for PBD), and to the blocked poly(N-PMI) (3-4.5 ppm, CH and 6.5-7.5 ppm phenyl) are clearly observed. The percentages of N-PMI block copolymerized (Tab. 1) were calculated from the area ratios of phenyl protons of N-PMI to methylene protons of each prepolymer.

The results mentioned above indicate that the novel block copolymer of POE/poly(N-PMI) and PBD/poly(N-PMI) are synthesized from anionic polymerization of N-PMI by initiation of the macromolecular alkoxides which is prepared by the modification of prepolymers possessing hydroxyl groups.

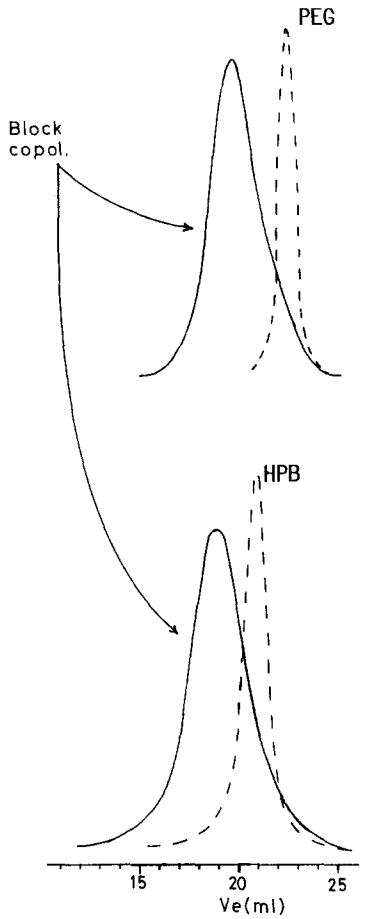


Fig. 1 GPC eluograms of block copolymers (solid line) and prepolymers (dotted line): POE/poly(N-PMI) (top; Run 2 in Tab.1) and PBD/poly(N-PMI) (bottom; Run 5 in Tab. 1).

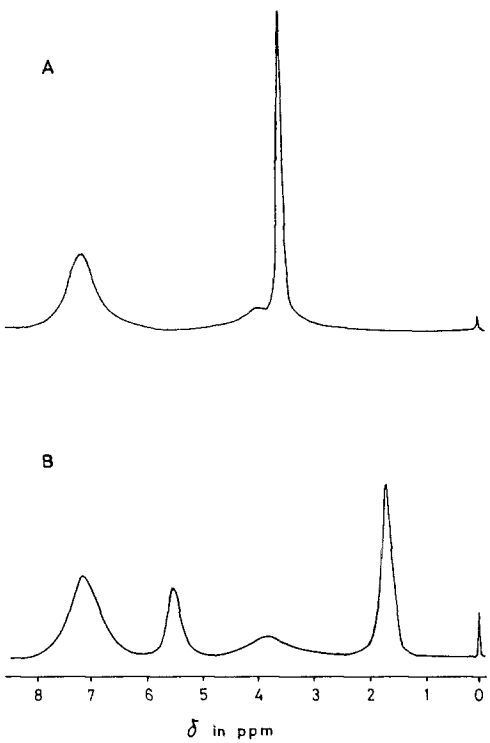


Fig. 2 ^1H NMR spectra of block copolymers: POE/poly(N-PMI) (**A**, Run 1 in Tab. 1) and PBD/poly(N-PMI) (**B**, Run 5 in Tab.1).

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