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. 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.

**Measurements**: 

1H 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 F254 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 prepolymer 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