Controlled/Living RAFT Polymerization of *N*-Phenyl Maleimide and Synthesis of Its Block Copolymers

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ABSTRACT: The controlled/living radical polymerization of *N*-phenyl maleimide (NPMI) was achieved using 2,2′-azobisisobutyronitrile as the initiator and 2-cyanopropyl-2-yl dithiobenzoate as the reversible addition-fragmentation chain transfer agent at 75°C in dichloroethane/ethylene carbonate (60/40, w/w) mixed solvent. The block copolymers of polystyrene-*b*-polyNPMI and poly(*n*-butyl methacrylate)-*b*-polyNPMI were successfully prepared by chain extension from dithiobenzoate-terminated polystyrene and poly (*n*-butyl methacrylate) to NPMI, respectively. The obtained NPMI-based (co)polymers were characterized by gel permeation chromatography and ^{1}H-NMR spectroscopy. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2469–2473, 2009

Key words: *N*-phenyl maleimide; RAFT polymerization; block copolymer; heat-resistant polymer

INTRODUCTION

Polymers of *N*-phenyl maleimide (NPMI) have excellent chemical and thermal stability with high glass transition temperature because of their polar and rigid five-membered imide ring structure.[1] NPMI is also useful as a heat-resistant modifier for common vinyl polymers.[2] These imide-based materials have been found to have versatile applications in industries ranging from aerospace to the medical and microelectronics fields.[3]

The (co)polymerizations involving NPMI has thus stimulated great interest in the last three decades, many methods have been reported to polymerize NPMI and to copolymerize it with other vinyl monomers, including radical polymerization, anionic polymerization, photoinduced polymerization, atom transfer radical polymerization, etc.[3] However, the reports on the controlled/living polymerization of NPMI were quite limited. To the best of our knowledge, only one article dealt with the "living" anionic polymerization of NPMI with alkali-metal *tert*-butoxides in the literature, which gave NPMI homopolymers with a maximum number-average molecular weight (M_n) of 9300 and relatively broad molecular

weight distributions (MWD, $\sim$ 1.26–1.36).[4] On the other hand, although many studies have been reported on the conventional and/or living copolymerizations of NPMI with common monomers such as (meth)acrylates, styrene (St), and its derivatives,[1] less work has been carried out on the preparation of block copolymers having polyNPMI as block units.[5]

In this article, we dealt with the controlled/living radical polymerization of NPMI, and furthermore the block copolymerizations with St and *n*-butyl methacrylate (*n*-BMA), via reversible addition-fragmentation chain transfer (RAFT) process. NPMI-based block copolymers may exhibit both excellent thermal resistance and mechanical properties as well as good solubility and melt processibility. They can be useful as additives for improving thermal resistance of other resins,[5,6] as compatibilizers for polymer blends,[5] or as precursors of a new kind of polyimide foams with a fairly low dielectric constant.[7] Moreover, block copolymers consisting of covalently bound polyNPMI (a "rigid" chain) and "soft" chains, such as poly(*n*-BMA), are expected to exhibit unique solution, solid-state, and interfacial properties. These copolymers have potential applications as novel thermoplastic elastomers and "rod–coil" block copolymers, which stimulated great interest in the last decade.[7]

EXPERIMENTAL

Materials

NPMI was prepared by the reaction of maleic anhydride and aniline according to the literature

method.[8] 2-Cyanopropyl-2-yl dithiobenzoate (CPDB) was synthesized and characterized according to the literature procedure.[9] n-BMA (purity >99%) and St (purity >99%) were purified by passing them through neutral alumina and silica gel columns, respectively, and distilled twice under reduced pressure over CaH_2 before use. Ethylene carbonate (EC, purity >99%) was used as received. Dichloroethane (DCE, purity >99.9%) was distilled twice over P_2O_5 and then over CaH_2 before use. Azobisisobutyronitrile (AIBN; purity >99%) was recrystallized twice from methanol.

RAFT polymerization of NPMI in the presence of CPDB

For a typical solution polymerization, a stock solution comprising NPMI (0.87 g, 5 mmol), AIBN (3.3 mg, 0.02 mmol), CPDB (11.1 mg, 0.05 mmol), DCE (3.8 g), and EC (2.6 g) was prepared and transferred to an ampule in a N_2-filled dry glovebox, and then degassed with three freeze-pump-thaw cycles, sealed, and heated at 75°C. After the predetermined interval, the sealed ampule was cooled in an ice bath, and the reaction mixture was diluted with DCE and then poured into a large amount of methanol. The precipitated polymer was washed with methanol and dried to constant weight under vacuum at 40°C; the monomer conversion was determined gravimetrically.

Preparation of block copolymers of NPMI

For a typical example of chain-extension experiment, a stock solution of DCE (6 mL) comprising NPMI (1.04 g, 6 mmol), AIBN (3.3 mg, 0.02 mmol), and dithiobenzoate-terminated polySt (0.50 g, 0.06 mmol; $M_n = 8300$, MWD = 1.13), obtained with CPDB/AIBN, was prepared and transferred to an ampule in a N_2-filled dry glovebox, and then degassed with three freeze-pump-thaw cycles, sealed, and heated at 75°C. After the predetermined interval, the sealed ampule was cooled in an ice bath, and the reaction mixture was poured into a large amount of methanol. The precipitated polymer was washed with methanol and dried to constant weight under vacuum at 40°C; the monomer conversion was determined gravimetrically.

Measurements

^{1}H-NMR spectra were recorded in $CDCl_3$ at room temperature on a Varian Unity Inova 300 spectrometer. The molecular weights and MWD were measured by gel permeation chromatography (GPC) against polystyrene standard in THF at a flow rate of 1.0 mL/min at 35°C on three Waters Styragel columns (meas-

urable molecular weight range: 100–5000, 500–30,000, and 5000–600,000) connected to a Waters 1515 pump and a Waters 2414 refractive index detector.

RESULTS AND DISCUSSION

RAFT polymerization of NPMI

For molecular weight control, controlled/living radical polymerization is the most effective procedure. The widely used controlled/living radical polymerization processes have been nitroxide-mediated polymerization, atom transfer radical polymerization, and more recently, RAFT polymerization. Because of its compatibility with a wide range of monomers and reaction conditions, the RAFT process appears considerably more versatile than other processes.[10] For the possible controlled/living RAFT radical polymerization of NPMI, it was polymerized using AIBN as the initiator and CPDB as the RAFT agent in DCE/EC (60/40, w/w) mixed solvent at 75°C ([NPMI]$_0$ = 1.0M; [NPMI]$_0$/[CPDB]$_0$/[AIBN]$_0$ = 250/2.5/1). In this study, EC was found to have good solubility to homopolymers of NPMI. However, it is inconvenient because it has a relatively high melting point, and the reaction mixture thereof was quite viscous. Therefore, a common solvent, DCE, was added as a cosolvent. The preliminary exploration demonstrated that the DCE/EC (60/40, w/w) mixed solvent showed good performance as reaction medium for the polymerization of NPMI. CPDB was chosen here as the RAFT agent because of its versatility for many RAFT controlled systems, especially for the polymerizations of (meth)acrylates.[11]

The RAFT polymerizations of NPMI were found to proceed smoothly with fairly high monomer conversions. The structure of the polymers was analyzed by ^{1}H-NMR spectroscopy (Fig. S1 in Supporting Information), which confirmed the formation of homopolymers of NPMI with the polymer chain ends capped with the RAFT agent fragment.

Figure 1 shows the rate for the RAFT polymerization. Figure 2 shows the corresponding plots of the M_ns and MWDs of the obtained polymers against the monomer conversions. The polymerization followed nearly first-order kinetics up to about 65%; and the M_ns increased linearly with the monomer conversions, and the MWD curves were quite narrow (MWD = 1.08–1.29), although they became slightly broader as the polymerization proceeded. These results indicated the "living" nature of the RAFT copolymerization. However, when the conversion of NPMI was over ∼ 65%, the polymerization mixtures turned viscous and opaque, which became more pronounced with the increase of the conversion, and eventually led to gel-like product (in 60 h, conversion ∼ 93%).
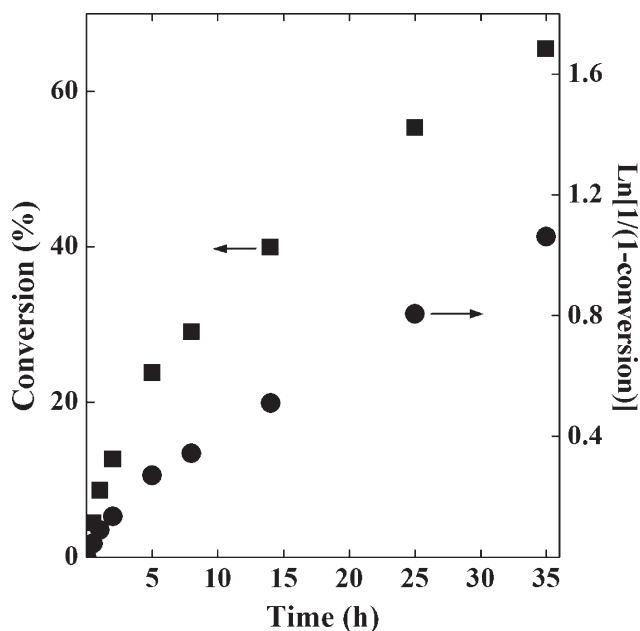
Figure 1 Time conversion (■) and semilogarithmic kinetics (●) plots for the polymerization of NPMI with AIBN as the initiator and CPDB as the RAFT agent in DCE/EC mixed solvent (60/40, w/w) at 75°C; [NPMI] =1.0M; [NPMI]$_0$/[CPDB]$_0$/[AIBN]$_0$ = 250/2.5/1.

Preparation of block coplymers of NPMI

To obtain block copolymers of NPMI, the dithiobenzoate-terminated polyNPMI (M_n = 4530, MWD = 1.25) obtained with CPDB/AIBN was used as the macro-RAFT agent for chain extension with St via RAFT process, AIBN as the initiator, and DCE/EC (60/40, w/w) mixture as the solvent (at 75°C; [St]$_0$ = 1.0M; [St]$_0$/[macro-RAFT agent]$_0$/[AIBN]$_0$ = 450/4.5/1). The reaction was rather slow, with the conversion of St being only 2.5% for 24 h. The GPC trace of the resulting copolymer was bimodal, that is, in addition to the main peak ($M_n \sim$ 5570, MWD $\sim$ 1.31), there appeared a small bump on the higher molecular weight side ($M_n \sim$ 464,200), which may be assignable to the homopolymer of St. Obviously, the chain extension from polyNPMI to St was not successful with a low blocking efficiency. This may be due to, in part, the fact that the macroradicals derived from NPMI were less active when compared with those from St. On the other hand, the morphology of dithiobenzoate-terminated polyNPMI may be unfavorable for the chain-extension reaction because solubility of polyNPMI in the DCE/EC (60/40, w/w) mixed solvent was not good. This may be explained from the fact that the chain-extension reaction from dithiobenzoate-terminated polyNPMI to NPMI itself was not highly efficient (Fig. S2 in Supporting Information).

Therefore, the chain extension from polySt to NPMI was attempted for a possible high blocking efficiency. To this end, well-defined dithiobenzoate-terminated homopolymers of St, with high and low molecular weights, were prepared from the polymerization using CPDB as the RAFT agent and AIBN as the initiator, and then chain extended with NPMI. The chain-extension reactions were performed in DCE at 75°C. The experimental conditions and results are listed in Table I (Entries 1–4). These results show that the M_ns of the chain-extension products shifted clearly toward the higher range, with the MWDs remaining low (below 1.3). Figure 3 shows the GPC traces of representative chain-extension products (Entries 1 and 2, Table I) obtained in the block copolymerizations of NPMI using low-
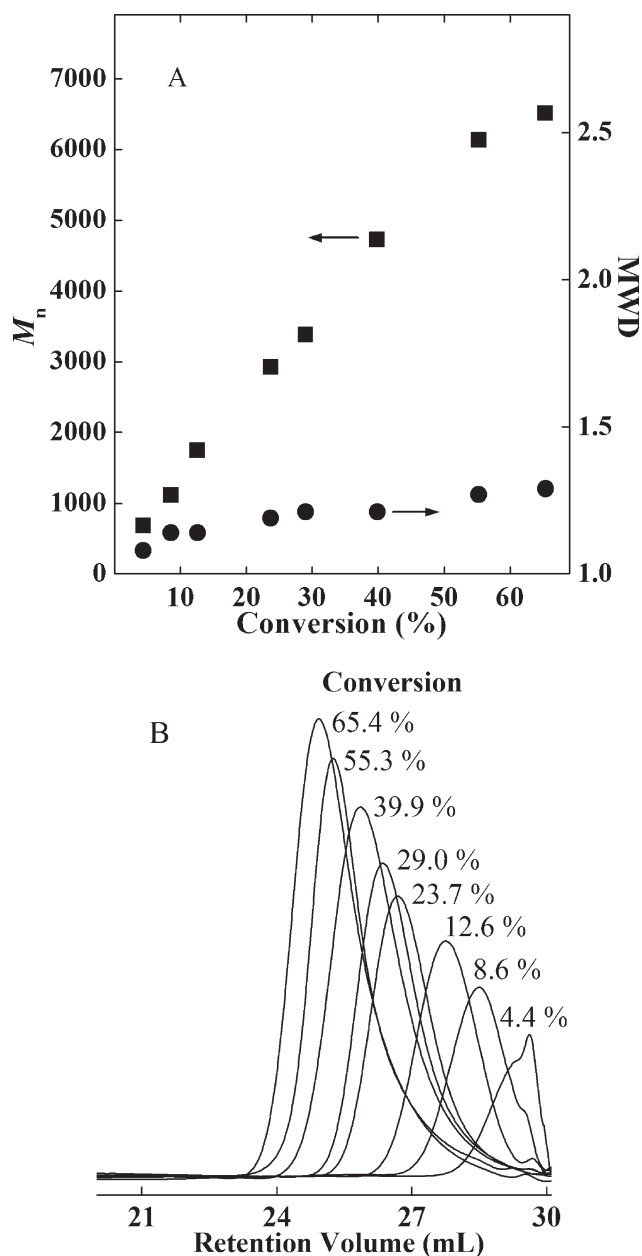

Figure 2 (A) M_n and MWD values and (B) MWD curves for the polymers obtained in the same experiments as for Figure 1.

TABLE I
Block Copolymerizations of NPMI and St or BMA via RAFT Process[a]

Entries	Macro-RAFT agent[b]/M_n (MWD)	Time (min)	Conversion (%)	M_n (MWD)[c]
1	PolySt/8300 (1.13)	15	10.1	9,530 (1.12)
2	PolySt/8300 (1.13)	160	41.5	11,700 (1.16)[d]
3	PolySt/16,800 (1.10)	60	30.0	20,400 (1.09)
4	PolySt/16,800 (1.10)	480	65.8	28,120 (1.15)[d]
5	Poly(n-BMA)/8800 (1.17)	10	8.0	10,860 (1.13)
6	Poly(n-BMA)/8800 (1.17)	250	51.5	17,470 (1.28)[d]
7	Poly(n-BMA)/15,050 (1.16)	20	13.1	17,500 (1.13)
8	Poly(n-BMA)/15,050 (1.16)	250	51.9	27,500 (1.26)[d]

[a] Polymerization conditions: in DCE; at 75°C; [NPMI] = 1M, [NPMI]$_0$/[Macro-RAFT agent]$_0$/[AIBN]$_0$ = 300/3/1.
[b] All prepared with AIBN/CPDB.
[c] Measured by GPC.
[d] The values shown are excluding the high-molecular-weight hump.

molecular-weight dithiobenzoate-terminated PSt ($M_n \sim$ 8300, and MWD $\sim$ 1.13) as the macro-RAFT agent. As shown, the M_ns and MWD values of the extension products were 9530 and 1.12 for 15 min (NMPI conversion $\sim$ 10.1%), and 11,700 and 1.16 for 160 min (NMPI conversion $\sim$ 41.5%), respectively. Moreover, the polymerization mixture in DCE remained homogeneous throughout the reaction, indicating the absence of homopolymers of NPMI which is essentially insoluble in DCE. These results demonstrate that the chain extension from PSt to NPMI could be well controlled and provided block copolymers with narrow MWD. It is noteworthy that, however, in the cases of the chain-extension products obtained at relatively high conversions of NPMI, the GPC traces of the resulting copolymers were bimodal, that is, in addition to the main peaks, there appeared small humps on the higher molecular weight range (e.g., $M_n \sim$ 96,900 for the sample product of Entry 2, Table I), the intensity of which increased with the monomer conversion, although their nature is still unknown (Fig. 3S in Supporting Information).

The structure of the copolymers was then analyzed by ^{1}H-NMR spectroscopy. Figure 4 shows the ^{1}H-NMR spectrum of a typical sample (Entry 3, Table I; $M_n \sim$ 20,400, MWD $\sim$ 1.09) obtained in the block copolymerization of NPMI using dithiobenzoate-terminated PSt ($M_n \sim$ 16,800, MWD $\sim$ 1.10) as the macro-RAFT agent. The spectrum showed distinct characteristic signals of the methyl protons (*a*),
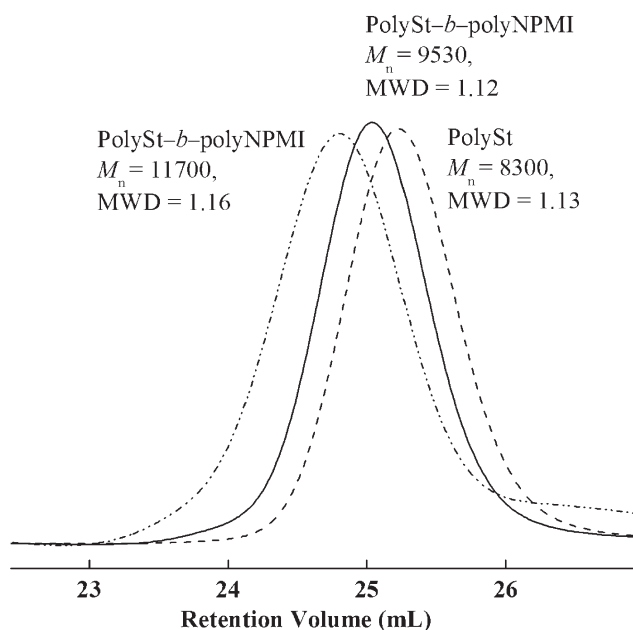

Figure 3 GPC traces of polySt (dash line) and polySt-*b*-polyNPMI after chain extension reactions with NPMI in DCE at 75°C for 15 min (solid line) and 160 min (dash dot line), respectively; [NPMI] = 1.0M, [NPMI]$_0$/[Macro-RAFT agent]$_0$/[AIBN]$_0$ = 300/3/1.
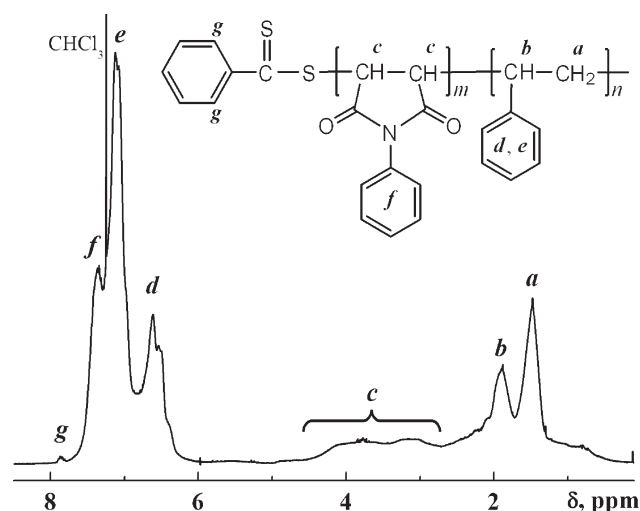

Figure 4 ^{1}H-NMR spectrum of a representative polySt-*b*-polyNPMI obtained in the same experiment as for Entry 3, Table I.

the methine protons (*b*), and the phenyl protons (*d*, *e*) from the polySt blocks, and the characteristic absorptions of the methine protons (*c*) and phenyl protons (*f*, overlapping partly with *e*) of the NPMI units in the polyNPMI blocks. In addition to these large absorptions, there appeared small absorptions at around 7.8 ppm, which were assignable to the *ortho*-phenyl protons (*g*) of the dithiobenzoate moiety derived from CPDB.[12] Therefore, the ^{1}H-NMR analysis further confirmed the formation of block copolymers of St and NPMI, and the copolymer chain end was capped with the RAFT agent fragment as expected according to the well-known mechanism of the RAFT process.[10]

Likewise, block copolymers of poly(*n*-BMA)-*b*-polyNPMI were sucessfully prepared by chain extension from poly(*n*-BMA) to NPMI. Herein, well-defined dithiobenzoate-terminated homopolyers of *n*-BMA, with high and low molecular weights, were prepared from the polymerizations using CPDB as the RAFT agent and AIBN as the initiator. The polymerization conditions and results are listed in Table I (Entries 5–8). The GPC and ^{1}H-NMR analyses (Figs. S4 and S5 in Supporting Information) demonstrated that the chain extension from poly(*n*-BMA) to NPMI could be well controlled and provided corresponding block copolymers with narrow MWD.

CONCLUSIONS

In conclusion, the controlled/living radical polymerization of NPMI was achieved for the first time using AIBN as the initiator and CPDB as the RAFT agent at 75°C in DCE/EC (60/40, w/w) mixed solvent. The block copolymers of polySt-*b*-polyNPMI and poly(*n*-BMA)-*b*-polyNPMI were successfully prepared by the block copolymerizations of NPMI using dithiobenzoate-terminated polySt and poly(*n*-BMA), respectively, as the macro-RAFT agent.

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