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SYNTHESIS OF A-B-A TYPE BLOCK COPOLYMER OF METHYL METHACRYLATE AND STYRENE BY LIVING FREE-RADICAL POLYMERIZATION†

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ABSTRACT

A newly synthesized iniferter, *N,N′*-dimethyl-*N,N′*-bis(phenethyl)-thiuram disulfide, has been used in the free-radical living polymerization of styrene by a photochemical method. The low molecular weight (M_w = 6000) difunctionalized polystyrene was used as a macroiniferter to photopolymerize methyl methacrylate, and was fractionated to obtain an A-B-A type block copolymer containing two poly(methyl methacrylate) units and one polystyrene unit in each block. The glass transition temperature, thermal stability, and ^{13}C NMR of the block copolymer are discussed.

INTRODUCTION

Radical polymerization is a very useful method for the large-scale preparation of various vinyl polymers. More than 70% of the vinyl polymers have been industrially produced by this method, which has a number of merits arising from the characteristics of intermediate free radicals. However, these radical polymerizations, performed mainly by azobisisobutyronitrile (AIBN) or benzoyl peroxide, have the problem of controlling the structure of the resultant polymers, i.e., the

†Dedicated to the memory of Dr. Gilbert Clouet.

control of the reactivity of the monomer. It is important to design polymers with well-controlled molecular weights, sequences, end groups, blocks, etc. In the radical polymerization of many monomers, though initiation occurs from the fragments of the free-radical generator, termination by disproportion and chain transfer reactions to the compound occurs also, and hence the initiator fragment per polymer molecule ratio is always less than 2. On the other hand, if an initiator (R—R′) has high chain transfer reactivity, a polymer with two initiator fragments can be obtained as

$$R{-}R' + nM \longrightarrow R{\left(M \right)}_n R'$$

These radical polymerizations may simply be considered as an insertion of monomer molecule into the R—R′ bond, similar to the telomerization of ethylene with carbon tetrachloride [1, 2]. It is well known that iniferters have such properties, which have been exploited to synthesize difunctional polymers both thermally and photochemically. These difunctional polymers may further be used as free-radical catalysts (macroiniferters), thus implying their usefulness as living polymers similar to living ionic polymerization. Among the iniferters used, mainly tetraethylthiuram disulfide has been reported to serve as a photoiniferter for the synthesis of block copolymers [3-7]. Otsu et al. reported some block copolymers such as polystyrene-*b*-polymethyl methacrylate [8], polystyrene-*b*-polyvinyl acetate [9], and polystyrene-*b*-polyvinyl alcohol [9] by such techniques. More recently, A-B-A type block copolymers of polystyrene by tetraethylthiuram disulfide have been reported [10]. However, very few have been explored using new types of dithiocarbamates in this regard.

In our previous report we described the synthesis of a new iniferter, *N,N′*-dimethyl-*N,N′*-bis(phenethyl)thiuram disulfide, and its successful use as a thermal free-radical initiator [11]. This paper describes the synthesis of difunctional polystyrene and an A-B-A type of triblock copolymer composed of two polymethyl methacrylate blocks and a polystyrene block by photochemical polymerization.

EXPERIMENTAL

Materials

The monomers, styrene (Sty) (Aldrich) and methyl methacrylate (MMA) (Atochem), were purified by a standard procedure [12]. Toluene was purified by a standard method, and was distilled prior to polymerization. All other common solvents were used as received.

N,N′-Dimethyl-*N,N′*-bis(phenethyl)thiuram disulfide (DPDT) was prepared as before and fully characterized by ^{1}H, ^{13}C NMR, UV, IR spectra, and elemental analysis [11].

Synthesis of Functionalized Polystyrene

Styrene (3 mL, 0.026 mol), toluene (7 mL) and DPDT (0.0417 g, 1×10^{-4} mol) were taken into a tube, degassed thrice, and transferred to a photocell (UV transparent) under argon. It was polymerized, 30 cm away from UV light (160 W) through an IR filter, at room temperature for 24 hours. The product was precipitated into methanol, and twice reprecipitated from toluene with methanol. Yield: 5.4%.

^{1}H NMR ($CDCl_3$): Phenyl (7.1 and 6.5 ppm, broad); backbone CH—, CH_2— (1.86–1.2 ppm, broad); catalyst fragments (2.8–4.3 ppm, small peaks).

Synthesis of Block Copolymer

Methyl methacrylate (2 mL, 0.0187 mol) and functionalized polystyrene (macroiniferter) (0.101 g) were degassed three times, transferred to a photocell under argon, and polymerized for 14 hours as above. The very high viscous copolymer solution was diluted with toluene, precipitated in methanol, filtered, washed, and dried under vacuum at 60°C. Yield: 38%.

The copolymer was further purified as follows: 0.5 g of the crude product was stirred with 25 mL acetonitrile overnight and filtered. It was further refluxed with cyclohexane for 6 hours, filtered, washed, and the copolymer was dissolved in toluene and precipitated in methanol. After drying, it gave 85% recovered pure block copolymer.

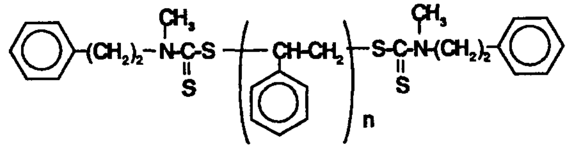
^{1}H NMR ($CDCl_3$): Phenyl (7.1 and 6.5 ppm); $-OCH_3$ of PMMA (3.65 ppm, s) and polymer backbone of PSty and PMMA (2.1–0.7 ppm). IR spectrum: —CO of PMMA (1720–1740 cm^{-1}).

Measurements

Infrared (IR) spectra were recorded using a Perkin-Elmer 983 spectrophotometer using polymer films on AgCl plates. ^{1}H- and ^{13}C-NMR spectra were recorded in a 200-MHz (50 MHz for ^{13}C) Bruker AC-200 Spectrometer in $CDCl_3$ solvent. The glass transition temperature (T_g) was determined using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of 20°C/min. The thermogravimetric analysis (TGA) was carried out by a Mettler TA3000 thermal analyzer in nitrogen atmosphere at a rate of 10°C/min. Molecular weights of the polymers and block copolymers were determined by a Waters GPC model 200 equipped with UV (254 nm) and Refractive Index (RI) detectors using tetrahydrofuran as eluent, and calibration with PMMA or PSty standards.

RESULTS AND DISCUSSION

Earlier studies on the mechanism of the free-radical polymerization of Sty and MMA by tetraethylthiuram disulfide indicate that the resulting polymers have two dithiocarbamate groups in each polymer chain [13], and these end groups are capable of further initiating block copolymerization [8, 9]. Recently we reported the thermal bulk polymerization of MMA by DPDT, in which the molecular weight of the polymer has been found to increase with the time of polymerization [11], indicating that it proceeds via a living polymerization mechanism. Thus, the polymers prepared by DPDT should contain two dithiocarbamates per molecule. Specifically it is true for low conversion, and low molecular weight polymer is obtained by using a high concentration of dithiocarbamate. In the photochemical polymerization of Sty by DPDT, the conversion was limited to only 5%, and the molecular



SCHEME 1.

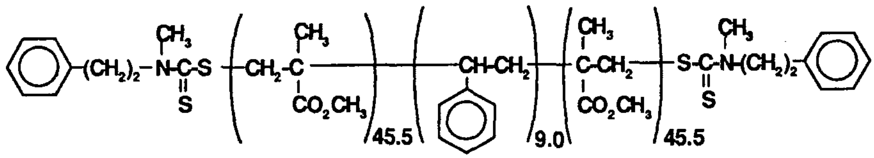
weight was controlled to about 6000, which indicates that the resulting polymer is a difunctional macroiniferter with the structure shown in Scheme 1.

^{1}H-NMR and IR spectra were in agreement with the formation of the polymer containing the dithiocarbamate groups. Interestingly, the GPC curves showed distinct differences between the UV and RI traces. The M_w, M_n, D (polydispersity), and M_p (peak average) molecular weights were 5000, 2800, 1.8, and 3600 for UV trace, and 7000, 3700, 1.90, and 8200 for RI trace. Though difference between M_p values are quite high, it is not unexpected due to the presence of UV-sensitive phenethyldithiocarnbamate groups in the polymer chain ends.

Block copolymer was prepared from MMA and PSty (macroiniferter) by bulk photopolymerization. The GPC trace of the crude product showed a peak in the low molecular weight region corresponding to unreacted PSty and a peak with a side hump due to the PMMA-PSty-PMMA triblock, and PMMA-*b*-PSty. It contains approximately 80% tri- and 20% di-block as measured from the relative ratio of the peak area. Purification by hot cyclohexane partially removed the di-block as observed in the GPC curve (10% di- and 90% tri-block). Complete separation of the di-block, however, remained a problem. The M_w, M_n, and D (polydispersity) of the purified block copolymer were 150,000, 36,000, and 4.17, respectively. The approximate composition of the block copolymer, as determined from ^{1}H NMR (from the relative ratio of $-OCH_3$ of the MMA unit, and phenyl of the Sty unit, considering the end phenyl functional group to be negligible in the high molecular weight block copolymer), was 9% PSty and 91% PPMA. Ideally, the block composition may be presented as in Scheme 2.

The block copolymer was further characterized by ^{13}C NMR. Figure 1 shows the spectrum. The peaks were tentatively assigned according to References 14 and 15. It reveals that PMMA unit is purely random, as normally found in radical polymerization. Since the molecular weight of the block is very high, $-C=S$ peak observed at 193 ppm in DPDT, i.e., the end functional group is not observed in the spectrum.

The glass transition temperature (T_g) of the block copolymer was determined to be 122°C, which is high as compared to the PMMA (105°C) and PSty (100°C)



SCHEME 2.

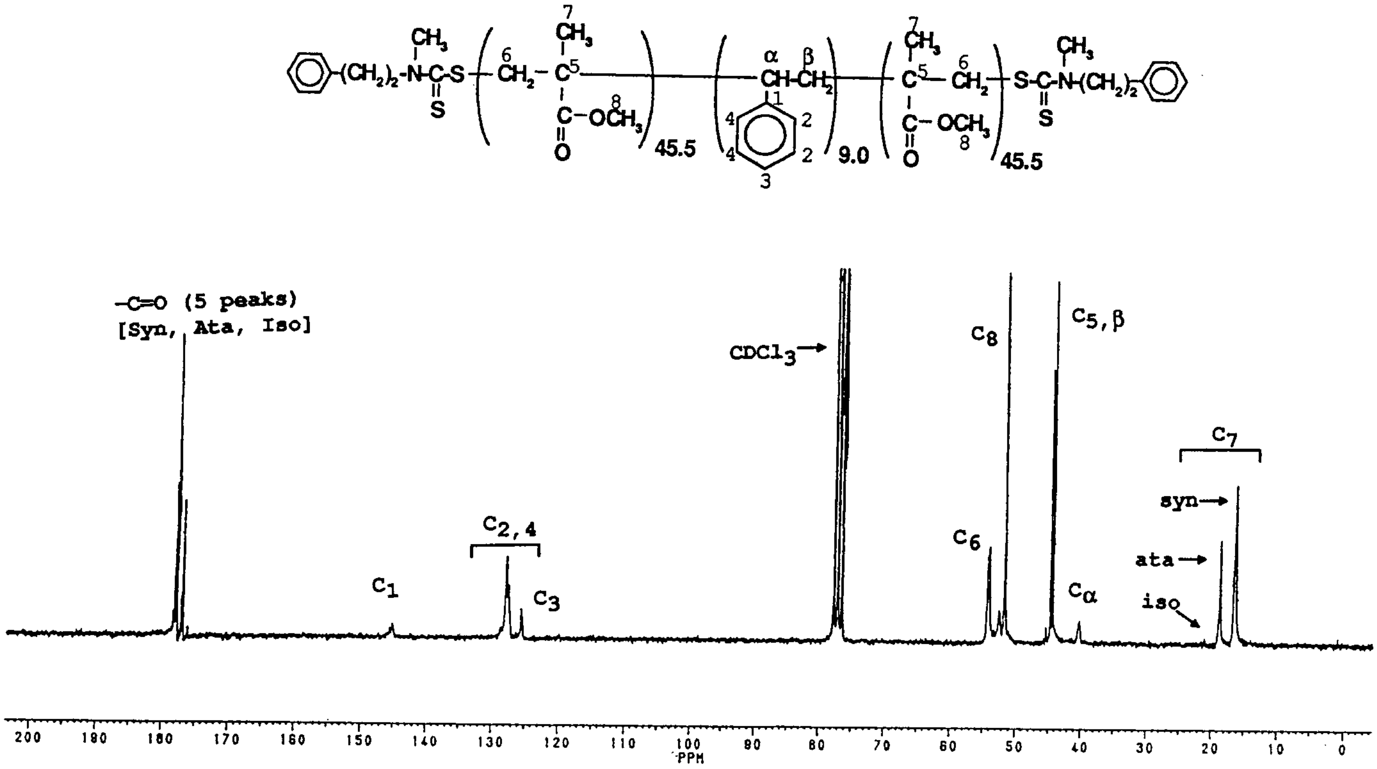


FIG. 1. ^{13}C-NMR spectrum of the block copolymer prepared by DPDT.

TABLE 1. Comparative Thermal Decomposition[a] Characteristics of Block Copolymer

	Weight loss at temperature °C					
Sample	10%	20%	40%	60%	80%	Complete
PMMA[b]	250	275	325	355	375	420
PSty[c]	330	355	365	395	410	520
Block[d]	295	310	320	330	345	380

[a] Heating rate, 10°C/min; nitrogen atmosphere.

[b] Prepared by azobisisobutyronitrile.

[c] Prepared by DPDT.

[d] Block copolymer, PMMA-PSty-PMMA, composition: 9% PSty, 91% PMMA.

homopolymers. The reason for such an unusual property of the tri-block is not known at the moment.

Table 1 shows the comparative weight loss of block copolymer and of PSty prepared by DPDT and PMMA by AIBN. Decomposition of PMMA occurred in two steps, whereas PSty and the block copolymer decomposed in a single step. The block copolymer was shown to be a stable intermediate of PSty and PMMA.

CONCLUSION

Difunctional polystyrene may be synthesized by *N,N'*-dimethyl-*N,N'*-bis-(phenethyl)thiuram disulfide, which acts as a macroiniferter. A-B-A type block copolymers of PMMA-PSty-PMMA can be prepared from such a macroiniferter. It may be possible to synthesize hydrophilic-hydrophobic-hydrophilic block copolymers by this PSty macroiniferter using suitable monomers, but this remains to be explored.

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