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Step-Growth Polymers as Macroinitators for "Living" Radical Polymerization: Synthesis of ABA Block Copolymers

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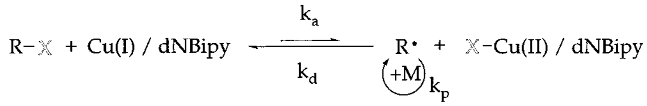
The synthesis of well-defined block copolymers between step-growth and vinyl polymers has been difficult to obtain due to the nature of the respective polymerization mechanisms. Many methods have been developed to bridge these differences.[1,2] These methods involve either the chain-growth or the step-growth polymer being prepared first. The synthesis of the chain-growth polymer first requires that the polymer have one or two functional groups at the chain ends. Using monofunctional chain-growth polymers in a step growth polymerization results in an ABA block copolymers with A = chain- and B = step-growth polymer; difunctional polymers result in $-[AB]_n-$ polymers. The preparation of telechelic chain-growth polymers can be accomplished by using "living"/controlled polymerizations, or through the use of transfer agents.[3] The use of "living"/controlled polymerizations would be preferred, so as to control the molecular weight and molecular weight distribution of the chain-growth polymer and to avoid the synthesis of polymers with a degree of functionality less than desired.[4] However, reactions between the telechelic polymer and the growing step-growth polymer may be difficult to bring to completion, resulting in incomplete block copolymer formation.

Preparation of step-growth polymers first requires the incorporation of terminal, lateral, or in-chain functional groups which can be activated to initiate a chain polymerization.[5−8] These chain polymerizations are generally radical in nature so as to prevent side reactions between the propagating chain and the functional groups in the step growth polymer. The use of terminal functional groups yields ABA block copolymers, while the use of lateral groups produces graft copolymers. When in-chain functional groups, such as azo or peroxy groups, are used, the step-growth polymer is broken into pieces upon decomposition of the functional groups. The resulting active centers then initiate the polymerization of the vinyl monomer; the result is the formation of ABA block copolymers if termination is by disproportion. If termination is by coupling, then polymers of the structure, $-[AB]_n-$ can be formed. The problem faced in this method is that the length of the step-growth polymer is determined by the random distribution of the functional groups and the rate at which they decompose. Also, by the nature of a free radical polymerization, the vinyl blocks are ill-defined and a homopolymer of the vinyl monomers can be formed as a result of transfer.

The use of terminal/lateral groups to prepare ABA/graft copolymers has been used by many groups. Particularly, Bamford and Eastmond have used alkyl halides to prepare graft and block copolymers by radical polymerization.[5,9−14] The polymerizations were initiated by formation of a carbon-centered radical by redox reaction between the alkyl halide and dimanganese decacarbonyl. The vinyl blocks prepared in such a manner were ill-defined, and generally there was incomplete block formation. Here we report the use of a "living" radical polymerization to prepare block copolymers between a step-growth polymer (polysulfone) and vinyl monomers with well-defined blocks.

Scheme 1



The advent of "living" or controlled radical polymerizations has promised to solve the above problems.[15−18] The "living" radical polymerization technique that has been used here is atom transfer radical polymerization, ATRP.[19−22] This process involves the activation and deactivation of a propagating chain end as a result of the reversible atom transfer reaction between a metal salt and alkyl halides, Scheme 1. The metal used in this paper was copper(I) bromide complexed with 4,4′-(5-nonyl)-2,2′-bipyridine (dNBipy). ATRP has been used for a variety of monomers such as styrenes, (meth)acrylates, and acrylonitrile to produce polymers with narrow molecular weight distribution ($M_w/M_n < 1.4$) whose molecular weight is defined by $M_n = \mathrm{MW} \times \Delta[\mathrm{M}]/[\mathrm{I}]_o$.

Step-growth polymers with activated halogen end groups were used as macroinitiators for ATRP. Polymers with two halogen end groups (for ABA block copolymers) could be prepared by simple adjustment of the monomer ratio or through the use of monofunctional monomers. To demonstrate the synthesis of a macroinitiator, polysulfone with phenolic end groups was used. The vinyl monomers used to prepare the block copolymers were styrene and butyl acrylate.

Polysulfone was prepared by the condensation polymerization of bisphenol A and 4,4′-difluorosulfone,[23] with bisphenol A in slight excess to prepare a polymer with phenolic end groups.[24] Low-molecular weight polymers were prepared to more easily discern the end groups by ^{1}H NMR. The macroinitiator was prepared by treating the polysulfone with 2-bromopropionyl bromide in the presence of pyridine. The degree of functionality appeared to be quite high as the molecular weight determined by SEC (THF, relative to styrene standards, $M_n = 4480$, $M_w/M_n = 1.5$) was in close agreement with that determined by ^{1}H NMR ($M_n = 4030$) through analysis of the end groups. Analysis of the ^{1}H NMR spectra, Figure 1, also shows that the conversion of the phenolic end groups (−OH, 6.7 ppm) of 2-bromopropionyloxy groups ($-CH_3$, 1.95 ppm) was quantitative, as their molar concentrations were the same.

The ABA block copolymers of polysulfone (B) with either styrene or butyl acrylate (A) were prepared by ATRP.[25] The conversion of the polymerizations after 6.75 h at 110 °C was found to be as follows: styrene, 67%, and butyl acrylate, 95%. The resulting polymers were confirmed as block copolymers after examination of the SEC traces (Figure 2) and ^{1}H NMR spectra of the polymers. Because the rate of the thermal initiation of styrene has been shown to be slow in comparison with ATRP, the amount of homopolymer of the vinyl monomers is assumed to be negligible.[19]

SEC of poly(styrene-*b*-sulfone-*b*-styrene) and poly(butyl acrylate-*b*-sulfone-*b*-butyl acrylate) showed that the copolymer peaks had shorter retention times than the macroinitiator and therefore had higher molecular weights. It is interesting to note that the molecular weight distributions of the two copolymers were narrower than the initial macroinitiator; styrene: M_w/M_n

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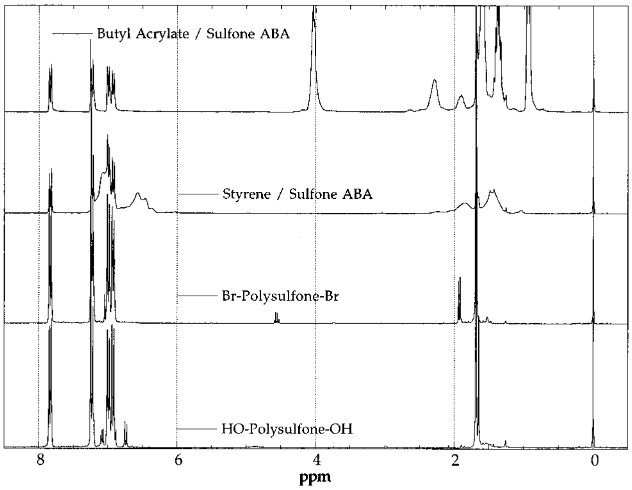

Figure 1. ^{1}H NMR spectra of polysulfone polymers and copolymers.

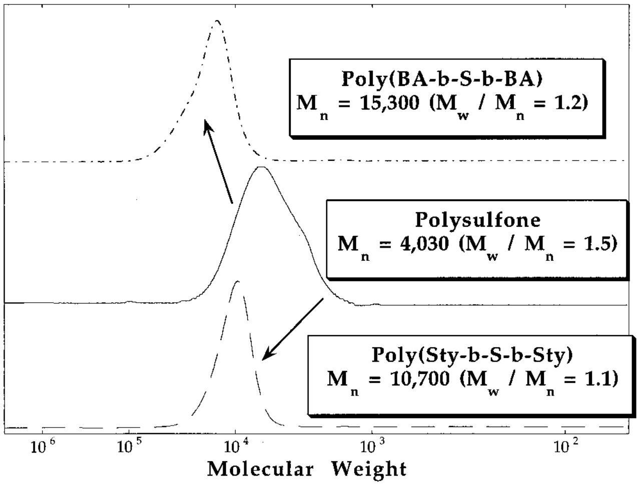

Figure 2. SEC traces of polysulfone macroinitiator and polysulfone block copolymers with styrene and butyl acrylate. SEC was performed in THF using linear polystyrene standards (x axis); reported M_n values were determined by ^{1}H NMR.

$= 1.1$, butyl acrylate: $M_w/M_n = 1.2$. This was due to the well-defined side blocks prepared by ATRP.

The molecular weights of the copolymers were estimated by ^{1}H NMR, Figure 1. For the butyl acrylate copolymer, the molar ratio of the $-\mathbf{CH_2}-$OC(O) to the aromatic protons of polysulfone was found to be $r = 11$. The product of r and the degree of polymerization of polysulfone ($DP_B = 8$) yielded the overall degree of polymerization for butyl acrylate ($DP_{2A} = 88$). This was in good agreement with the expected degree of polymerization as defined by $DP = \Delta[BA]/[I]_o = 95$. The total molecular weight of the copolymer was $M_n = 15\ 300$. Similar examination of the ^{1}H NMR spectrum for the styrene copolymer; Figure 1, yielded a total molecular weight of $M_n = 10\ 700$; the degree of polymerization of styrene was $DP_{2A} = 64$, whereas the expected value, assuming quantitative initiation, was $DP = \Delta[Sty]/[I]_o = 67$.

Thermal analysis of the copolymers demonstrated the presence of the two block copolymers. DSC of the polymers displayed two T_gs: styrene copolymer; 104 °C (styrene), 159 °C (polysulfone); butyl acrylate copolymer; −41 °C (butyl acrylate), 153 °C (polysulfone). Thermal gravametric analyses, TGA, Figure 3, were performed in air and displayed a distinct shoulder corresponding to the higher thermal stability of the polysulfone than the blocks of the vinyl monomers. The phase behavior of these films and the mechanical properties of higher molecular weight materials are currently being studied.

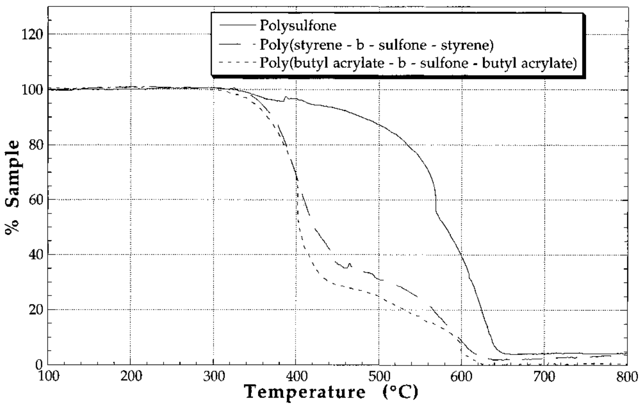

Figure 3. TGA (in air) data for block copolymers of polysulfone and styrene or butyl acrylate.

The synthesis of well-defined block copolymers of a step-growth polymer, polysulfone, and the vinyl monomers styrene and butyl acrylate has been demonstrated. The macrointiator was prepared by conversion of the polysulfone's phenolic end groups to α-haloesters. This macrointiator was then used to initiate the polymerization of styrene or butyl acrylate by ATRP. The polymerization of the two vinyl monomers was shown to cleanly yield block copolymers with novel physical properties.

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(24) **Synthesis of Polysulfone:** In a 300 mL, three-neck flask with a Dean−Stark trap and condenser, bisphenol A (5.36 g, 23.5 mmol) and bis(4-fluorophenyl) sulfone (5.0 g, 19.9 mmol) were dissolved in a solution of *N*,*N*-dimethylacetamide (60 mL) and toluene (40 mL). Potassium bicarbonate (8.13 g, 58.8 mmol) was then added. The reaction was stirred at 140 °C for 3.5 h. The reaction was then heated to 170 °C for 12 h. Water was collected in the Dean−Stark trap as an azeotropic mixture with toluene. The reaction was then cooled and precipitated into water/methanol (50:50). The resulting polymer was reprecipitated from THF into water/methanol (2×) and then dried. Mass: 7.5 g. Yield: 79 %.

(25) **Synthesis of Copolymers:** To a 10 mL round-bottom flask with magnetic stir bar was added the macroinitiator (1.0 g, 0.25 mmol), dNBipy (202.4 mg, 0.5 mmol), CuBr (36.1 mg, 0.25 mmol), and 1,4-dimethoxybenzene (1.0 g). The flask was sealed with a rubber septum and the contents degassed by applying a vacuum and backfilling with argon (3×). Degassed monomer (Sty, 2.8 mL, 24.8 mmol; BA, 3.6 mL, 24.8 mmol) was then added via syringe. The reaction mixture was heated in a thermostated oil bath (110 °C) while stirring. After 6.75 h, the reaction was cooled and purified by repeated precipitation from THF into MeOH/brine.

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