Notes

Polymer-Bound Metal-Free Carbanion as Initiator for Controlled Grafting of Acrylic Polymers†

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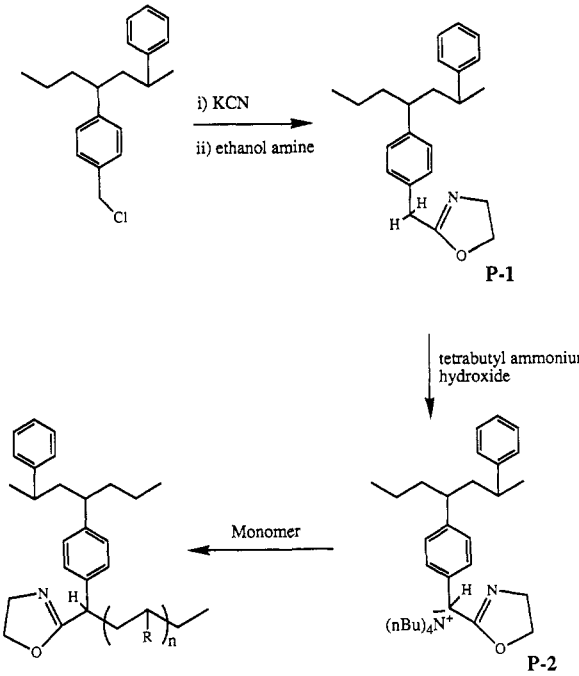
Modification of polymeric materials by grafting with functional polymer chains has been a subject of fundamental and practical importance.[2,3] The traditional approach to graft polymer formation involves free-radical polymerization. Excepting few examples,[4] this process is devoid of any control over the amount of grafting and length of the grafted polymer chain.[5] Recent interest in design of polymers possessing sophisticated architecture[6] (viz., comb, brush, hyperbranched polymer structures, etc.) requires development of synthetic protocols for grafting of polymer chains in a controlled manner onto the backbones of initial materials (base polymers).

The technique of anionic polymerization is an elegant method for generating macromolecular chains with predicted molecular weight and narrow molecular weight distribution, for manipulating polymer chain end to subsequent reactions, etc.[7] Classical anionic initiators such as metal alkyls require low-temperature operation. In particular, polymerization of acrylic monomers with such initiators has been less satisfactory and requires special manipulations.[8] We, Reetz et al., and, more recently, Seebach et al. have reported the use of metal-free carbanions as anionic initiators for polymerizing acrylic monomers in a controlled manner at room temperature.[9–11] Use of the organic countercation as the soft counterion has been considered to be responsible for such interesting behavior of these initiator systems.[12] The attractive features of this new anionic initiator system prompted us to develop functional polymeric supports carrying such metal-free carbanions to initiate polymerization of acrylic monomers. This approach would result in controlled grafting of such polymer chains on the original polymer supports. While polymeric supports for the synthesis of biopolymers such as polypeptides, polynucleotides, and polysaccharides are well known in the literature,[13] controlled synthesis of vinyl polymers on polymer supports has been explored to a lesser extent.[14,15]

We considered polymer-bound benzyloxazoline **P-1** as the target precursor for the polymeric carbanion. The low molecular weight analog (namely, 2-benzyloxazoline) of this polymer gave a satisfactory result as the initiator for the polymerization of acrylic monomers.[9] A two-step chemical modification procedure was adopted to synthesize this functional polymer. A linear copolymer of styrene and 4-vinylbenzyl chloride (copolymer composition, 6:4 mol:mol) was converted to a copolymer of styrene and 4-vinylbenzyl nitrile by treating with potassium cyanide under phase transfer conditions.[16] This benzyl nitrile-containing copolymer was transformed to the benzyloxazoline-bearing copolymer **P-1** by treating the former with ethanolamine at 70 °C for 8 h under nitrogen. The polymer **P-1** thus obtained gave satisfactory spectral analysis results. Polymer-bound carbanion **P-2** was generated by treating 0.14 g of polymer **P-1** in 20 mL of dry THF with 0.3 mmol of tetrabutylammonium hydroxide under an argon atmosphere. The reaction mixture was allowed to warm to 60 °C and was kept at this temperature for 6 h. The appearance of a red coloration suggested formation of the polymer-bound carbanion carrying tetrabutylammonium ion as the countercation. After removal of the solvent under reduced pressure and drying of the polymer in vacuo for several hours, a stock solution of this polymeric initiator in dry THF was prepared and stored under an inert atmosphere. This carbanion solution is stable for several weeks at ambient temperature. Anionic polymerization of acrylic monomers using this polymeric initiator was brought about by slow addition of an excess of monomer to **P-2** in THF at room temperature. Initiation of polymerization was evident by a rise in temperature of the reaction medium and disappearance of the red coloration of the initiator solution. Reaction pathways ranging from synthesis of the polymer-bound benzyloxazoline to grafting of acrylic polymer chains onto this polymeric carrier are illustrated in Scheme 1.

Scheme 1



R = COOMe, COOtBu, COOnBu or CN

We have tested the polymerization ability of three different acrylic monomers, viz., *n*-butyl methacrylate (nBMA), *tert*-butyl methacrylate (tBMA), and acrylonitrile (AN), initiated by this polymeric carbanion at room temperature. All three monomers polymerized successfully, resulting in grafting of these chains on the functional styrene copolymer backbone. Purification of graft copolymers was performed by repeated precipitation using

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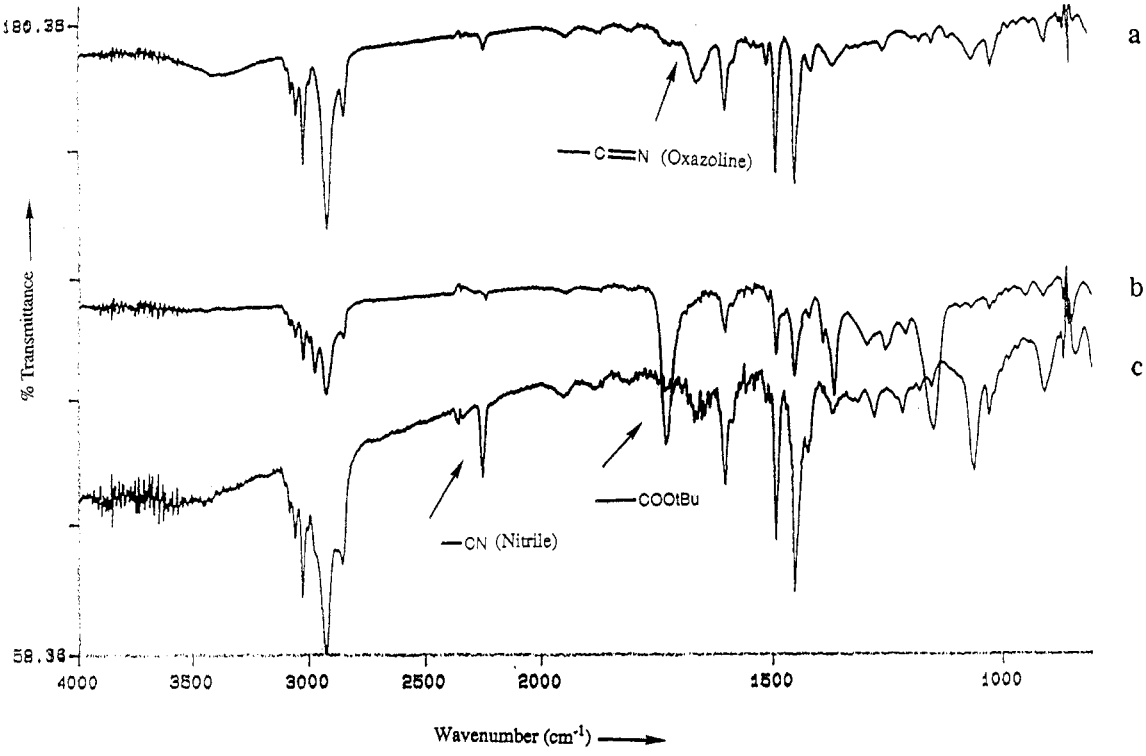

Figure 1. Infrared spectra of (a) polymer **P-1**, (b) polymer **P-1** grafted with tBMA, and (c) polymer **P-1** grafted with AN.

Table 1. Characterization of Graft Copolymers Obtained by Using Polymeric Metal-Free Anionic Initiator

entry	monomer used for grafting onto **P-1** anion	M_n[a]	M_w/M_n[a] (PDI)	grafting efficiency[b]	% grafting[c]	chem shifts of important carbon atoms of the polymers (in ppm)
1	*d*	18 000	1.92			39.8, 41.5–44.2, 52.8, 68.5, 126.2–130.0, 146.2, 168.4
2	nBMA	25 000	1.85	16.2	71.2	peaks in entry 1 plus 16.0, 20.5, 33.4, 64.5, 175.2
3	tBMA	27 000	1.82	21.8	94.3	peaks in entry 1 plus 27.5, 36.5, 82.0, 172.5
4	AN	24 000	1.95	55.7	80.0	peaks in entry 1 plus 120.5

[a] Determined by GPC using monodisperse polystyrene as the primary standard. [b] Grafting efficiency = (weight of grafted copolymer)/(weight of monomer used for grafting) × 100. [c] % Grafting = [(weight of grafted copolymer) − (weight of homopolymer)]/(weight of homopolymer) × 100. [d] Polymer **P-1**, which is the precursor for the polymeric carbanion.

THF as solvent and methanol as nonsolvent.[17] Evidence for grafting of acrylic polymer chains to the functional polystyrene backbone was obtained by spectroscopic analysis of these copolymers. FTIR spectra of the benzyloxazoline-containing copolymer **P-1** (carbanion precursor) and the graft copolymers based on tBMA and AN are presented in Figure 1. The spectrum of the copolymer 1 (Figure 1a) shows the characteristic band due to the oxazoline C=N stretching at 1654 cm^{-1}. The spectra of the graft copolymers of tBMA (Figure 1b) and AN (Figure 1c) show the newer vibrational bands at 1734 (ester carbonyl) and 2245 cm^{-1} (nitrile), respectively, thus attributing to incorporation of these polymer chains onto the backbone of polymer **P-1**. The 1654-cm^{-1} vibrational band due to the oxazoline ring is also retained in the graft copolymers, which is more clearly evident in Figure 1c. ^{13}C NMR spectra of the graft copolymers also reveal additional resonance lines due to the new monomer units in addition to those due to the initial polymer **P-1**. Thus, in the case of tBMA grafted copolymer, characteristic ^{13}C resonance lines at 175 and 28 ppm due to ester carbonyl carbon and methyl carbon atoms, respectively, are clearly evident. Chemical shifts of different carbon atoms appearing in the spectra of these copolymers are summarized in Table 1.

Gel permeation chromatography (GPC) of these copolymers provides the most convincing evidence for covalent grafting of the acrylic polymer chains onto the backbone of polymer **P-1** (which acts as the macromolecular anionic initiator). The precursor polymer **P-1** possesses a number-average molecular weight (M_n) 18 000 with a polydispersity index (PDI) of 1.92. The molecular weights of all the graft copolymers obtained were higher than this polymeric initiator (Table 1). Furthermore, the PDI of the graft copolymers remained unchanged (in the range 1.80–1.95). This clearly suggests the chemical linkage of the acrylic polymer chains to the polymeric initiator backbone. This finding also suggests the absence of any contaminating oligomeric species in the samples. The grafting efficiency ranged from 13 to 55%, whereas % grafting varied between 70 and 94% (Table 1).

We have demonstrated the generation of metal-free carbanion on a polymeric support which is capable of initiating polymerization of acrylic monomers at room temperature. The ability of such polymeric initiators to polymerize acrylic monomers in a controlled manner offers a novel means to design newer types of functional polymer architectures exhibiting interesting materials properties.

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