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Living Radical Polymerization Involving Oxygen-Centered Species Attached to Propagating Chain Ends†

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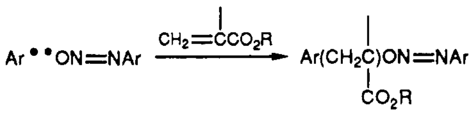
ABSTRACT: A new series of electron-transfer initiators has been shown to give rise to long-lived oxygen-centered radical species attached to propagating acrylate and methacrylate chain ends. The long-lived nature of these chain ends makes it possible, in some cases, to prepare block copolymers. The oxygen-centered radical species are generated from hyponitrite, arenediazoate, or cyanate anions by reaction with electron acceptors, such as arenediazonium ions or activated alkyl halides. Copolymers prepared from sequential polymerization of methyl acrylate, butyl acrylate, and methyl methacrylate were shown to consist largely of A–B blocks, based on GPC, LC, and ^{1}H NMR analyses. Reactions were carried out over a temperature range of 25–60 °C and in a variety of solvents.

Introduction. An increasing number of reports of syntheses of polymers with complex architecture has appeared, such as block and graft copolymers and star polymers. Control of such architectures has largely been achieved using group-transfer[1] and living anionic[2] or cationic[3] techniques. A longstanding goal has been the development of practical living radical polymerization methods. A most notable example of living radical polymerization involves the "iniferter" concept developed by Otsu[4] which takes advantage of sulfur-centered radicals, such as dithiocarbamate groups. Carbon-centered radial end groups based on arylmethanes have also been examined by Otsu[4] and Braun[5]. Despite considerable progress, a truly living radical polymerization system has not yet been developed.[6] In this report we describe a new series of electron-transfer initiators which give rise to long-lived oxygen-centered radical species attached to the propagating ends of acrylate and methacrylate polymers. In some cases, the long-lived nature of the oxygen-centered end groups makes it possible to prepare block copolymers.

Results and Discussion. Initiating species containing oxygen-centered radicals ($^\bullet$OY) can be generated in at least two ways. The first involves electron transfer between activated carbon–halogen compounds with arenediazoate anions. This gives rise to carbon-centered radicals which initiate monomer polymerization, and the arylazooxyl radical ($^\bullet$ON=NAr) which is associated with the growing end of the chain. For comparison, Kornblum showed that suitably activated alkyl halides undergo facile electron transfer when reacted with anions such as $(CH_3)_2C(NO_2)^-$, $C_6H_5S^-$, N_3^-, and 1-methyl-2-naphthoxide.[7] The second method involves one-electron oxidation of arenediazoate, hyponitrite, or cyanate anions by reaction with arenediazonium ions (eq 1). Aryl radicals then initiate polymerization of the monomer, and the corresponding stabilized oxyl radical is associated with the growing end of the polymer (eq 2).

$$\begin{array}{lll} ArN_2^+ + {}^-ON{=}NAr \rightarrow Ar^\bullet + N_2 & {}^\bullet ON{=}NAr & \\ \quad ({}^-ON{=}NO^-) & ({}^\bullet ON{=}NO^-) & \\ \quad ({}^-OCN) & ({}^\bullet OCN) & (1) \end{array}$$

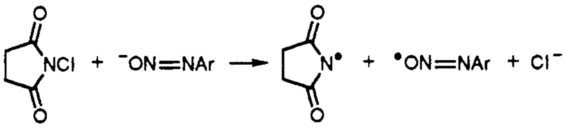


$$Ar^{\bullet}\,{}^{\bullet}ON{=}NAr \xrightarrow{CH_2{=}\overset{|}{C}CO_2R} Ar(CH_2\underset{CO_2R}{\overset{|}{C}})ON{=}NAr \qquad (2)$$

MMA was radically polymerized using PhN_2BF_4 and $Na_2N_2O_2$. The PMMA was purified by precipitating from THF with methanol, followed by precipitating from THF with hexane. The purified PMMA was found by ^{1}H NMR and fast-atom bombardment mass spectroscopy to contain C_6H_5 groups. Arylazooxyl radicals ($XArN{=}NO^\bullet$), generated by rearrangement of *N*-nitrosoacetamides, have been characterized by ESR.[8]

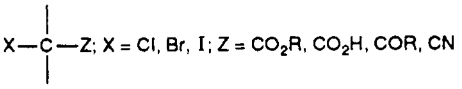
N-Halosuccinimides also react with arenediazoate, hyponitrite, or cyanate anions in the presence of monomer to initiate polymerization, presumably in analogy to the reactions using arenediazonium ions.

p-Nitrobenzoyl chloride, on the other hand, reacts with arenediazoate anions, but not with hyponitrite or cyanate anions, in the presence of monomer to initiate polymerization, in parallel with activated alkyl halides (eq 3). A possible explanation for the different behavior of arenediazoates versus hyponitrites and cyanates may have to do with the higher electrochemical oxidation potentials of hyponitrite (+0.9 V) and cyanate (>+1.4 V) compared with that of *p*-nitrobenzenediazoate (+0.75 V).[9]



(3)

Although we demonstrated polymerization of acrylates and methacrylates by reaction of arenediazoates with a variety of primary, secondary, or tertiary alkyl halides, living radical polymerization would be expected to occur only when activated alkyl halides are used. Suitably activated alkyl halides contain at least one α-electron-withdrawing group, such as an ester, acid, ketone, or nitrile group:



$$X{-}\underset{|}{\overset{|}{C}}{-}Z;\ X = Cl, Br, I;\ Z = CO_2R, CO_2H, COR, CN$$

A reasonable rationalization is that unactivated alkyl halides react preferentially with $O_2NC_6H_4N{=}NO^-$ to give relatively stable arylazo ether products[10] and initiate polymerization because of side reactions. Whereas arylazo

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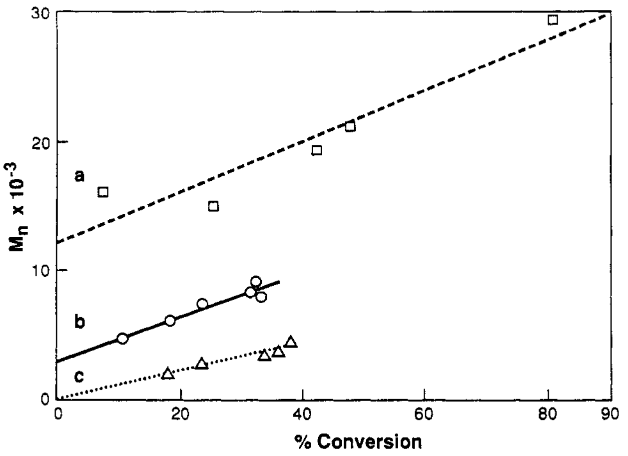


Figure 1. M_n as a function of conversion for polymerization of MMA using (a) ethyl 2-bromoisobutyrate (0.7 M), $O_2NC_6H_4N{=}NONa$ (0.07 M), MMA (7.0 M), and H_2O (7.8 M) at 25 °C; (b) $C_6H_5N_2BF_4$ (0.08 M), $O_2NC_6H_4N{=}NONa$ (0.08 M), MMA (7.9), and H_2O (8.7 M) at 25 °C; and (c) $C_6H_5N_2BF_4$ (0.06 M), $Na_2N_2O_2$ (0.03 M), MMA (6.2 M), and CH_3OH (8.2 M) at 40 °C.

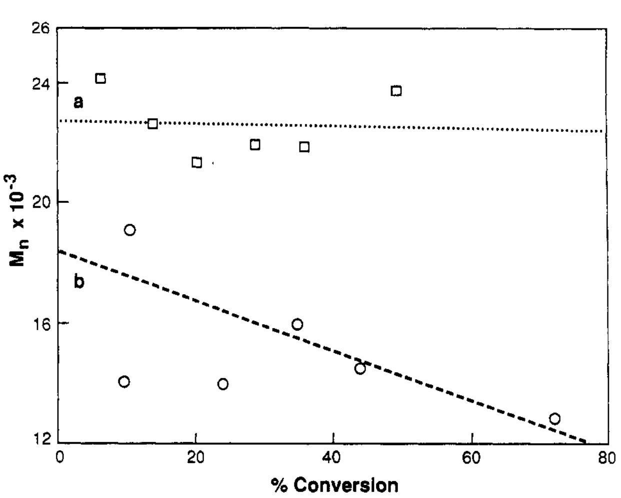
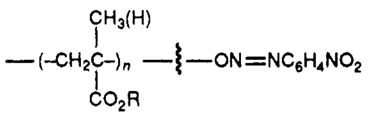


Figure 2. M_n as a function of conversion of polymerization of MMA using (a) $O_2NC_6H_4CH_2Cl$ (0.08 M), $O_2NC_6H_4N{=}NONa$ (0.08 M), MMA (7.8 M), and H_2O (8.7 M) at 25 °C; and (b) CH_3I (0.73 M), $O_2NC_6H_4N{=}NONa$ (0.07 M), MMA (7.3 M), and H_2O (9.7 M) at 35 °C.

ethers with unactivated R groups [ArN=NOR, R = alkyl] are thermally quite stable,[11] analogous arylazo ethers with activated R groups have not been reported.[12]

Polymerization of acrylates or methacrylates can conveniently be studied at temperatures of 25–40 °C. At these temperatures, it is reasonable that the C–O bond of the growing end of polymer chains, formed by radical recombination (by analogy to Otsu's iniferter), would be weakened to allow for insertion of monomer units.



$$-(-CH_2\overset{CH_3(H)}{\underset{CO_2R}{C}}-)_n -\wr- ON{=}NC_6H_4NO_2$$

Homolysis of the O–N bond would lead to a terminal alkyloxyl group and would thus not exhibit living radical polymerization characteristics. An analogous system involving $^{\bullet}ONR_2$ radical end groups has been developed by Solomon but is operative at temperatures generally greater than bout 80 °C.[13]

The formation of the active initiating species for polymerization requires at least some intimate contact of the electron acceptors and oxyanions for polymerization to proceed at reasonable rates. This can be facilitated using small amounts of polar cosolvents, such as alcohols, ketones, nitriles, DMF, etc., or solubilizing agents such as polyethers. Tetraalkylammonium salts can also be used as phase-transfer catalysts to solubilize the sodium or potassium oxyanion salts. The systems are generally tolerant of water and can be run as aqueous emulsion polymerizations. A range of monomers, including acrylates, methacrylates, hydroxyethyl acrylate, *N*-phenylmaleimide, and chloroprene, has been successfully polymerized. However, the extent of conversion depends on the choice of solvent or cosolvent used with a particular electron acceptor/oxyanion combination.

Living Nature of Radical Polymerization Reactions. Two aspects of the reactions in general have been examined which indicate that significant portions of polymers produced are formed via living radicals mechanisms. First, M_n was found to increase with increasing conversion when polymerization reactions were carried out with either arenediazonium ions or activated alkyl halides as electron acceptors (Figure 1). Use of unactivated alkyl halides, such as CH_3I or $O_2NC_6H_4CH_2Cl$, does not lead to a positive correlation (Figure 2). The ratios of N_n/[initiation precursors], for the diazoate/$(CH_3)_2CBrCO_2Et$ initiator (Figure 1a), show that only a portion of the compounds form active initiator. Also, M_w/M_n ratios for PMMA and PBA prepared using the latter initiator are generally in the range of 3.0 or greater. Such broad polydispersities may indicate that rates of initiation are not significantly faster than propagation rates or that there is a continuous steady generation of initiating species. The diazonium ion systems, on the other hand, give polymers with M_w/M_n ratios generally in the range of 2.0–3.0.

The other feature indicative of a living nature is the demonstration that a polymerization can be interrupted, monomer removed under reduced pressure, a different monomer added, and polymerization continued. For example, an A–B block copolymer of methyl methacrylate (MMA) and butyl acrylate (BA) was prepared by allowing MMA (53 mmol) to react with $C_6H_5N_2BF_4$ (0.24 mmol), $Na_2N_2O_2$ (0.24 mmol), and 2 mL of methanol at 30 °C for 3 h. The resulting PMMA was vacuum stripped (0.1 mm) to remove methanol and unreacted MMA. A 0.42-g sample of the PMMA (M_w = 9220 and M_n = 2890) was then allowed to react with BA (3.6 mmol) and 2 mL of acetone at 30 °C for 3 h to yield a copolymer containing a BA/MMA ratio of about 1/4, based on ^1H NMR. GPC analysis of the poly(MMA–BA) product (Figure 3) gave M_w = 16 300 and M_n = 3900. LC analysis showed that the PBA/PMMA copolymer was largely block in nature, when compared with either PMMA or PBA homopolymers or a sample of PBA/PMMA random copolymer (Figure 4).

An A–B block copolymer of methyl acrylate (MA) and BA was also prepared by first allowing MA (22 mmol) to react with *N*-bromosuccinimide (0.45 mmol) and silver cyanate (0.45 mmol) in 2 mL of THF at 40 °C for 4 h. The resulting PMA was vacuum stripped to remove THF and unreacted MA, and a ^1H NMR analysis showed that no significant MA remained in the PMA. A 0.10-g sample of the PMA (M_w = 36 300 and M_n = 15 500) was then allowed to react with BA (7.2 mmol) and 1 mL of THF for 17 h at 40 °C to yield a copolymer containing a PMA/PBA ratio of 1/4.9 by ^1H NMR. GPC analysis gave M_w = 116 000 and M_n = 19 400. LC analysis showed that the polymer was highly block in nature, with a poly(MA–BA) to PMA ratio of 99.3/0.7 (Figure 5).

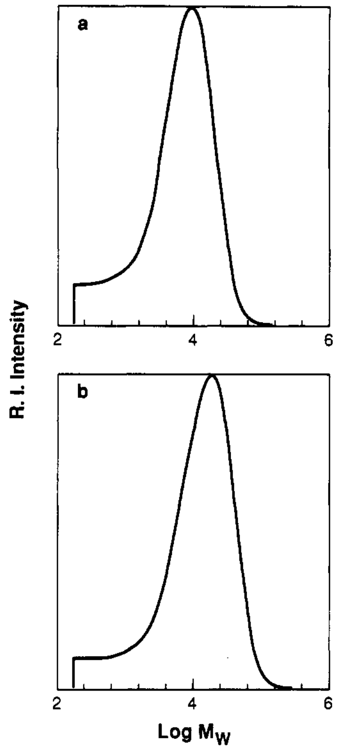


Figure 3. GPC chromatograms for (a) PMMA and (b) PBA/PMMA using a μstyragel column (Waters), THF solvent, RI detector, PMMA standards for calibration, and 25 °C.

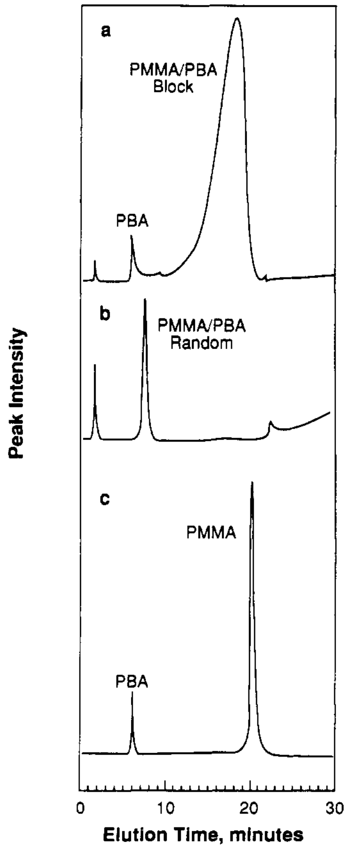


Figure 4. LC chromatograms for (a) PMMA/PBA block copolymer (4/1), (b) PMMA/PBA (0.63/1) random copolymer, and (c) PBA and PMMA homopolymers using an SI 60 column, light scattering detector, and toluene/methyl ethyl ketone solvent gradient.

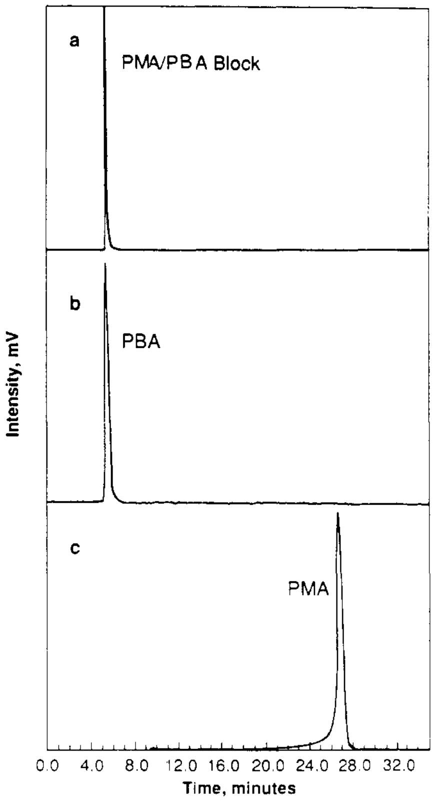


Figure 5. LC chromatograms for (a) PMA/PBA block copolymer (1/4.9), (b) PBA homopolymer, and (c) PMA homopolymer using an SI 60 column, light scattering detector, and toluene/methyl ethyl ketone solvent gradient.

Although not all combinations of initiators, solvents, and monomers were successfully used in preparing block copolymers, several did give quite clean block copolymers. These include *N*-bromosuccinimide and silver cyanate in THF at 40 °C with MMA, followed by BA; ethyl 2-bromoisobutyrate and $O_2NC_6H_4N{=}NONa$ in H_2O at 25 °C with MA, followed by BA; and $O_2NC_6H_4N_2BF_4$ and $Na_2N_2O_2$ in methanol at 30 °C with MA, followed by BA.

The details of these reactions will be published subsequently.

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(11) TGA measurements gave the following temperatures for 50% decomposition: $O_2NC_6N_4N{=}NOCH_3$, 308 °C; $O_2C_6H_4N{=}NOC_6H_{13}$, 225 °C; and $O_2NC_6H_4N{=}NOcyC_6H_{11}$, 170 °C.

(12) Under conditions where CH_3I or *tert*-C_4H_9Br react with $O_2NC_6H_4N{=}NONa$ to generate the arylazo ethers in good yield, $(CH_3)_2CBrCO_2C_2H_5$ is nearly unreactive.

(13) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U. S. Patent 4,581,429.

Registry No. (PMMA)(PBA) (block copolymer), 108501-18-4; PBA (homopolymer), 9003-49-0; (PMA)(PBA) (block copolymer), 115180-61-5; PMA (homopolymer), 9003-21-8; PMMA (homopolymer), 9011-14-7; CH_3I, 74-88-4; $O_2NC_6H_4CH_2Cl$, 115361-26-7; PhN_2BF_4, 369-57-3; $Na_2N_2O_2$, 100435-20-9; $O_2NC_6H_4N{=}NONa$, 136503-83-8; bromosuccinimide, 128-08-5; silver cyanate, 3315-16-0; ethyl 2-bromoisobutyrate, 600-00-0.