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A Strategy for Developing Novel Structural Polyurethanes and Functional Materials. Controlled/Living Free-Radical Polymerization of Acryloyl Azide under ^{60}Co γ-ray Irradiation

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The chemistry of azides and nitrenes has attracted the attention of chemists since the discovery of phenyl azide by Griess and the first proposal of nitrenes as reaction intermediates by Tiemann over 100 years ago.[1] Acyl azides are particularly useful intermediates in organic chemistry because they are readily transformed into isocyanates via Curtis rearrangement, sequentially into a variety of functional groups such as carbamates and ureas.[2] During the past decade, a number of very useful polymer materials, such as polyurethanes, polyureas, and polyamides, have been prepared based on azide chemistry.[3−9] Nishi and co-workers synthesized linear polyureas, polyurethanes, and polyamides by careful selection of the reaction substrate to acyl azides.[3−5] Okaniva et al.[9] reported a novel one-pot procedure for the synthesis of dendritic poly(amide−urea)s via the Curtis reaction. But the polymers involving acyl azide are almost prepared by the method of step polymerization. All of the polymers aforementioned are heteroatom chain polymers. On the other hand, carbon chain polymers with azido groups generally were synthesized by modification reaction of polymers.[10−13]

Polymer chemists continue to explore new methods of polymerization to obtain novel polymers with well-defined structures and high or functional performances using common and unique monomers. It is well-known that chain polymerization is a very powerful tool to synthesize the polymers especially with controlled molecular weight and well-defined structures.[14] Unfortunately, we noticed that quite a few papers were published on preparation of polymer by chain polymerization of unsaturated acyl azide as monomer. Singh et al.[15] once reported that the copolymerization of cinnamoyl azide and styrene was carried out at 90 °C, and the result product was styrene−styryl isocyanate copolymers other than azide polymer. It is obvious that azidocarbonyl group is easily transformed into isocyanate group under thermal condition. Recently, we were attracted by polymers with acyl azido groups since controlled/living free radical polymerization of unsaturated acyl azides as monomers seems to be a challenging idea. If possible, novel structural acyl azido polymers such as random copolymers, block copolymers, and star-shaped polymers with controlled molecular weight would be obtained. All of these polymers are useful precursors for the isocyanate polymers; thereby, we can prepare various unique polyurethanes and other functional materials under controlled conditions. Moreover, it would be expected that these polyurethanes may exhibit a variety of physical properties that are distinguishable from the conventional ones produced by step polymerization because of their different structures. In comparison with isocyanate prepolymers, acyl azide polymers are less sensitive to moisture, so a long shelf life is expected, which is very important in industry.

Acryloyl azide is the most simple vinyl monomer with azidocarbonyl group. However, until now, no information is available for its polymerization behavior. The probable reason is that it is neither suitable for ionic polymerization due to its structure nor for free radical polymerization because it is unstable under conventional polymerization condition; i.e., acyl azide may decompose or even explode in net form at temperature 20−100 °C or under UV conditions.[16] To our knowledge, there is no report involving the polymerization of vinyl acyl azide by chain polymerization without change of the azidocarbonyl groups during the process.

Recently we successfully achieved controlled/living free radical polymerizations of vinyl monomers under ^{60}Co γ-ray irradiation in the presence of dibenzyl trithiocarbonate[17−19] and dithiobenzoic acid[20] even if the γ-ray-initiated polymerization is generally very difficult to control. Later, Davis et al.[21−23] reported the living free radical polymerizations of styrene and methyl methacrylate and the graft polymerization of styrene onto polypropylene film under a constant source of γ-radiation. A remarkable advantage of the γ-ray irradiation living free radical polymerization is that the process can be performed at room temperature[17] or even lower temperature.[24] In the present study, we report a powerful method to prepare acyl azido polymers with no change of acyl azido groups via the controlled/living free radical polymerization of acryloyl azide under ^{60}Co γ-ray irradiation, which provide a promising strategy to develop novel structural polyurethanes and other functional materials.

Since acyl azides are sensitive to thermal and UV conditions, we considered that the key point of the γ-ray-initiated polymerization is the stability of acyl azide under ^{60}Co γ-ray irradiation. To examine the stability of acyl azide, model compounds such as propanoyl azide and benzoyl azide were synthesized according to the literature[16] for this study. Their benzene solutions were radiated for 300 min under the polymerization condition (60 Gy min^{-1}, 0 °C). The samples were characterized by FTIR on KBr tablet before and after irradiation. For propanoyl azide, the peaks at 2136.4 cm^{-1} arisen from $-N_3$ had almost no changes between samples before and after radiation. Similar results were obtained for benzoyl azide. The results indicated that aliphatic and aromatic acyl azides are stable at 0 °C during the radiation process.

Considering the stability of acryloyl azide in net form, we chose the copolymerization of methyl acrylate (MA) and acryloyl azide (AAz) for this study. AAz was first synthesized according to the related literature[16] and stored in a refrigerator prior to use. The polymerizations were performed in a sealed tube under ^{60}Co γ-ray irradiation (60 Gy min^{-1}) at 0 °C in the presence of *S*-benzyl-*O*-phenyl dithiocarbonate (BPDTC), which has been used in controlled/living free radical polymeriza-

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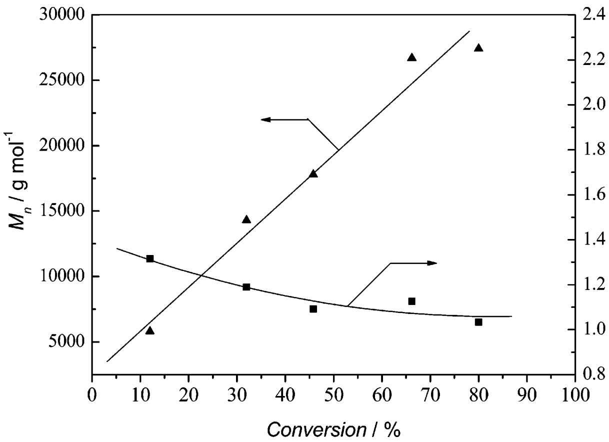

Figure 1. Molecular weight and molecular weight distribution as a function of monomer conversion for the polymerization (the initial concentration of *S*-benzyl-*O*-phenyl dithiocarbonate (BPDTC), $[\mathrm{BPDTC}]_0 = 0.125$ mol L^{-1}, and the molar ratio of methyl acrylate (MA) and acryloyl azide (AAz), $[\mathrm{MA}]_0/[\mathrm{AAz}]_0 = 9$ mol/mol).

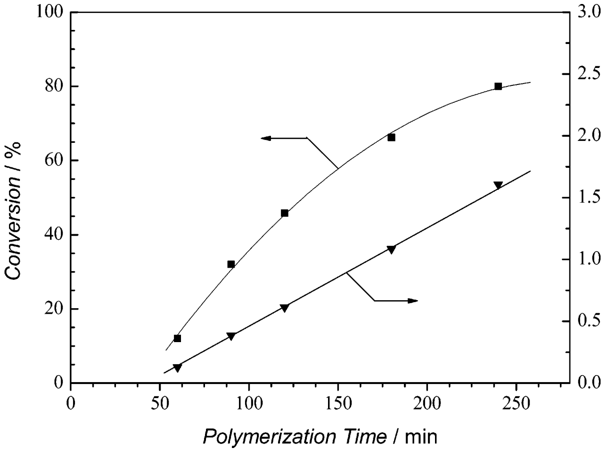

Figure 2. Conversion and $\ln([\mathrm{M}]_0/[\mathrm{M}])$ as a function of polymerization time for the polymerization (the initial concentration of *S*-benzyl-*O*-phenyl dithiocarbonate (BPDTC), $[\mathrm{BPDTC}]_0 = 0.125$ mol L^{-1}, and the molar ratio of methyl acrylate (MA) and acryloyl azide (AAz), $[\mathrm{MA}]_0/[\mathrm{AAz}]_0 = 9$ mol/mol).

tion of MA under γ-ray irradiation.[25] The mixture of monomers ($[\mathrm{MA}]_0/[\mathrm{AAz}]_0 = 9$ mol/mol) and BPDTC ($[\mathrm{BPDTC}]_0 = 0.125$ mol L^{-1}) was placed in a 5 mL polymerization tube. After it was degassed with performing a freeze−evacuate−thaw cycle three times, the tube was sealed under vacuum. Then it was placed in an insulated room exposed to a ^{60}Co source. After the polymerization, the reaction mixture was dissolved with THF and then precipitated in 10-fold *n*-hexane. The polymer was collected by filtration and dried under reduced pressure at room temperature (~10 °C).

The molecular weight of poly(MA-*co*-AAz) increases linearly with monomer conversion, and the polydispersity remains very narrow throughout the polymerization and becomes narrower with monomer conversion increasing (Figure 1). Figure 2 shows a linear relationship between $\ln([\mathrm{M}]_0/[\mathrm{M}])$ and polymerization time, which indicates that the polymerization is a first-order reaction with respect to monomer concentration and that the number of active radicals remains constant during the polymerization. All the evidences indicate that the polymerization is a “living” process. On the other hand, the plots in Figure 2 show that the polymerizations

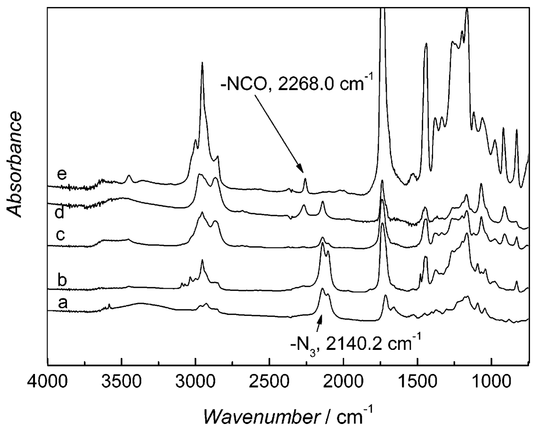

Figure 3. FTIR spectra of samples on KBr tablet: (a) monomer (acryloyl azide); (b) polymerization mixture (containing polymer, methyl acrylate, and acryloyl azide) after irradiation (60 Gy min^{-1}, 300 min); (c) polymer precipitation; (d) polymer dried at 20 °C for 48 h; (e) polymer dried at 40 °C for 12 h.

undergo some inhibition, which has been discussed elsewhere.[25]

Elementary analysis for the copolymer ($M_\mathrm{n} = 3900$ g mol^{-1}, conversion = 8.1%) has given the following values: C, 75.86; H, 9.12; N, 6.67%. The values are very close to the calculated values for ideal random copolymer ($C_{39}H_{57}O_3N_3$): C, 76.05; H, 9.33; N, 6.82%. The result shows that the polymerization may be an ideal copolymerization reaction, which should be attributed to the similar unsaturated structure of the monomers.

Our most important concern is the stability of acyl azido group during polymerization process. To examine the stability, the structures of the copolymers were characterized by FTIR spectra. It was noticed that the characteristic azidocarbonyl peak remained unchanged throughout the radiation process (Figure 3a−c). Furthermore, the sensitivity of the copolymer to temperature was investigated. It was found that the copolymer in THF solution remains stable for more than 6 months at 2 °C in a refrigerator. When stored at 20 °C for 48 h, it was observed that the intensity of peak for azidocarbonyl group (2140.2 cm^{-1}) began to decrease, and a new peak corresponding to isocyanate group appeared at 2268.0 cm^{-1} (Figure 3d). A similar phenomenon was observed when it was placed at 40 °C for 4 h.

The azidocarbonyl peak completely disappeared after a period of 12 h at 40 °C (Figure 3e). The polymers were characterized by ^{13}C NMR spectra (Figure 4). It can be clearly seen that a peak (128.2 ppm) for the carbon of isocyanate has occurred after a period of 12 h at 40 °C while the peak (182.2 ppm) corresponding to the carbon of acyl azide disappeared. The results demonstrated that azidocarbonyl group remained unchanged during the polymerization under γ-ray irradiation and that it can be easily transformed into isocyanate group via Curtis rearrangement under convenient controlled conditions.

In conclusion, the controlled/living free radical polymerizations of acryloyl azide and methyl acrylate were achieved under ^{60}Co γ-ray irradiation at 0 °C in the presence of BPDTC. Model experiments indicated that aliphatic and aromatic acyl azides were stable at 0 °C during the radiation process. The polymerization results indicated that the polymerization is a “living” free radical process. Elementary analysis for the copolymer showed that the polymerization is an ideal copolymerization reaction. The investigation of the stability of the

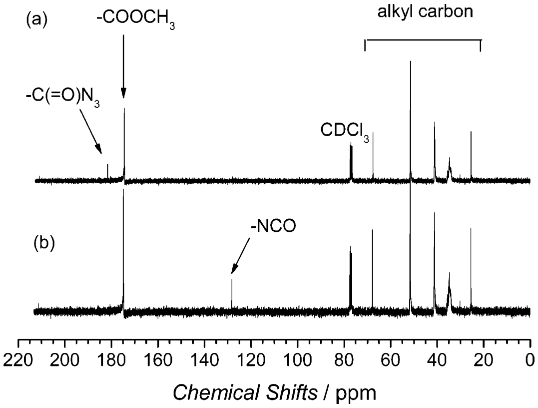

Figure 4. ^{13}C NMR spectra (300 MHz, CDCl$_3$) for the copolymers of methyl acrylate and acryloyl azide: (a) stored at 2 °C for 7 days and (b) dried at 40 °C for 12 h.

polymer revealed that azidocarbonyl group remains stable during the polymerization and can be transformed into isocyanate group via Curtis rearrangement by convenient control. To the best of our knowledge, this is the first report describing acryloyl azide used as a monomer in controlled/living free radical polymerization. This work indicated that polymerization initiated by γ-ray can be a strategy to design and prepare novel structural polyurethanes and other functional materials. Further extensive work is underway in our lab.

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