A Strategy for Synthesis of Azide Polymers via Controlled/Living Free Radical Copolymerization of Allyl 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[1] and the first proposal of nitrenes as reaction intermediates by Tiemann[2] over 100 years ago. Organic azides are particularly useful intermediates in synthetic chemistry because they are readily introduced into molecules and can be transformed into a variety of functional groups such as amines, azo compounds, etc.[3] During the past decade, new applications have been developed in polymer chemistry regarding the reactivity of nitrene that are generated when azides are decomposed thermally or photochemically. Because of the highly energetic decomposition of azides, azide-containing materials such as glycidyl azide polymers (GAP)[4−7] and bis-azide methyloxetane polymers (BAMO) [8−10] have been explored as binder materials that increase the burning rates of propellants. In addition, azide polymers are widely used for cross-linking,[11−14] and azide-based surface modifications have been used to improve the biocompatibility of prosthetic implants.[15−17]

However, since the azido group is sensitive to thermal and UV conditions, azide polymers are commonly prepared by chemical modification of polymers in biphase using sodium azide and chlorinated polymers in the presence of a phase transfer agent at lower temperature,[8,11,18−20] and some are obtained by living cationic ring-opening polymerization. Hsiue and co-workers[21] used 3-azidomethyl-3′-methyloxetane (AMMO) as the monomer in a triflic anhydride [$(CF_3SO_2)_2O$] initiating polymerization system and obtained well-defined block copolymers with various molecular weights and low polydispersity indexes. Talukder[22] achieved quasi-living cationic polymerization of AMMO with a bis(chlorodimethylsilyl)benzene/silver hexafluoroantimonate (BSB/$AgSbF_6$) initiating system in methylene chloride at −78 °C. However, ionic polymerization requires stringent reaction conditions such as high purity of monomers and low temperatures.

Controlled/living free radical polymerization is a promising alternate to ionic polymerization, as a radical process is more tolerant of functional groups and impurities, and can be carried out under relatively simple experimental conditions. However, until now, no information was available for free radical polymerization of vinyl azide monomer. The probable reason is that it is unstable under conventional free radical polymerization conditions (i.e., the azide group may decompose or even explode under thermal or UV conditions).

Recently, we had successfully achieved controlled/living free radical polymerizations of vinyl monomers under ^{60}Co γ-ray irradiation in the presence of dibenzyl trithiocarbonate[23] although the γ-ray irradiated polymerization is generally very difficult to control. The remarkable advantage of the γ-ray irradiation living free radical polymerization is that the polymerizations can be performed at room temperature[23] or even lower temperature.[24] In this paper, we report a strategy for synthesis of azide polymer via controlled/living free radical polymerization of allyl azide under ^{60}Co γ-ray irradiation in the presence of *S*-benzyl *O*-phenyl dithiocarbonate (BPDTC), which has been used to control the polymerization of methyl acrylate.[25]

Considering the stability of allyl azide in net form, we chose the copolymerization of allyl azide (AAz) with methyl acrylate (MA), styrene (St), and methyl methacrylate (MMA), respectively, for this study (see Supporting Information). The polymerization results listed in Table 1 show that molecular weight distributions are very narrow, and the experimental molecular weights agree well with the theoretical data, $M_{n,th}$, which is calculated by eq 1:

$$M_{n,th} = \text{conversion} \times (W_{comonomer} + W_{AAz})/M_{BPDTC} + M_{m,BPDTC} \quad (1)$$

where $W_{comonomer}$, W_{AAz}, and M_{BPDTC} are the weights of comonomer and AAz in the feed and the moles of BPDTC added, and $M_{m,BPDTC}$ is the mole mass of BPDTC.

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(1) Griess, P. *Philos. Trans. R. Soc. London* **1864**, *13*, 377.
(2) Tiemann, F. *Ber. Dtseh. Chem. Ges.* **1891**, *24*, 4162.
(3) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297−368.
(4) Parr, T.; Hanson-Parr, D. *Combust. Flame* **2004**, *137*, 38−49.
(5) Kim, E. S.; Yang, V.; Liau, Y. C. *Combust. Flame* **2002**, *131*, 227−245.
(6) Arisawa, H.; Brill, T. B. *Combust. Flame* **1998**, *112*, 533−544.
(7) Ger, M. D.; Hwu, W. H.; Huang, C. C. *Thermochim. Acta* **1993**, *224*, 127−140.
(8) Nair, J. K.; Satpute, R. S.; Polke, B. G.; Mukundan, T.; Asthana, S. N.; Singh, H. *Def. Sci. J.* **2002**, *52*, 147−156.
(9) Chang, T. C.; Wu, K. H.; Chen, H. B.; Ho, S. Y.; Chiu, Y. S. *J. Polym. Sci, Part A, Polym. Chem.* **1996**, *34*, 3337−3343.
(10) Kubota, N. *J. Propul. Power* **1995**, *11*, 677−682.
(11) Ruud, C. J.; Jia, J. P.; Baker, G. L. *Macromolecules* **2000**, *33*, 8184−8191.
(12) Jia, J. P.; Baker, G. L. *J. Polym. Sci, Part B, Polym. Phys.* **1998**, *36*, 959−968.
(13) Gonzalez, L.; Rodriguez, A.; de Benito, J. L.; Marcos-Fernandez, A. *J. Appl. Polym. Sci.* **1997**, *63*, 1353−1359.
(14) Varma, I. K. *Macromol. Symp.* **2004**, *210*, 121−1229.
(15) Marinucci, L.; Lilli, C.; Guerra, M.; Belcastro, S.; Becchetti, E.; Stabellini, G.; Calvi, E. M.; Locci, P. *J. Biomed. Mater. Res. Part A* **2003**, *67A*, 504−509.
(16) van der Heiden, A. P.; Willems, G. M.; Lindhout, T.; Pijpers, A. P.; Koole, L. H. *J. Biomed. Mater. Res.* **1998**, *40*, 195−203.
(17) Kuijpens, J. M. H.; Kardaun, G. A.; Blezer, R.; Pijpers, A. P.; Koole, L. H. *J. Am. Chem. Soc.* **1995**, *117*, 8691−8697.
(18) Brochu, S.; Ampleman, G. *Macromolecules* **1996**, *29*, 5539−5545.
(19) Sacristan, J.; Reinecke, H.; Mijangos, C. *Polymer* **2000**, *41*, 5577−5582.
(20) Gaur, B.; Lochab, B.; Choudhary V.; Varma, I. K. *J. Therm. Anal. Calorim.* **2003**, *71*, 467−479.
(21) Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S. *J. Polym. Sci. Part A, Polym. Chem.* **1995**, *33*, 1607−1613.
(22) Talukder, M. *Makromol. Chem.-Macromol. Symp.* **1991**, *42−3*, 501−511.

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Table 1. Copolymerization Results of AAz under ^{60}Co γ-ray Irradiation (60 Gy min^{-1})

entry[a]	comonomer	time (min)	conv. (%)[b]	$M_{n,th}$[c]	M_n[d]	M_w/M_n[d]	AAz incorp.[e] (mol %)
1	MA	60	8.0	4200	6000	1.15	5.0
2	MA	120	19.6	10300	10500	1.10	12.2
3	MA	360	56.5	29900	28800	1.07	17.9
4	St	1220	6.6	3500	3000	1.32	3.1
5	St	2660	16.6	8700	9600	1.29	7.6
6	MMA	150	28.3	14900	16200	1.16	8.7
7	MMA	320	60.0	31500	29500	1.09	16.5

[a] Each sample was prepared in benzene using a molar ratio between comonomer and AAz of 3 mol/mol, while [AAz] = 3.00 mol L^{-1} and [BPDTC] = 0.0188 mol L^{-1}. [b] Determined gravimetrically. [c] Calculated according to eq 1. [d] Determined by gel permeation chromatography (GPC), which was calibrated with polystyrene standard. [e] Calculated from elementary analysis.

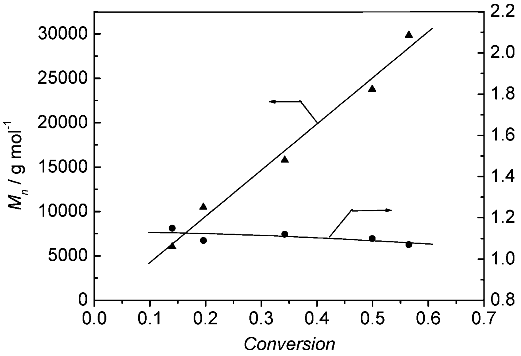

Figure 1. Molecular weight and molecular weight distribution as a function of monomer conversion for the copolymerization of AAz and MA.

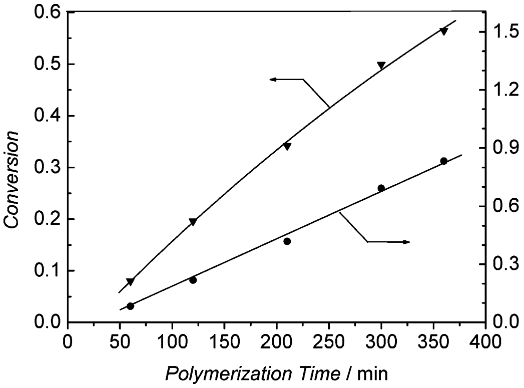

Figure 2. Conversion and ln([M]$_0$/[M]) as a function of polymerization time for the copolymerization of AAz and MA.

Figure 1 describes molecular weight and molecular weight distribution as a function of monomer conversion for the copolymerization of AAz and MA. It has been found that molecular weight of poly(AAz-*co*-MA) increases linearly with monomer conversion and that molecular weight distribution remains very narrow throughout the polymerization and becomes narrower with monomer conversion increasing. Figure 2 shows a linear relationship between ln([M]$_0$/[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 controlled/living process.

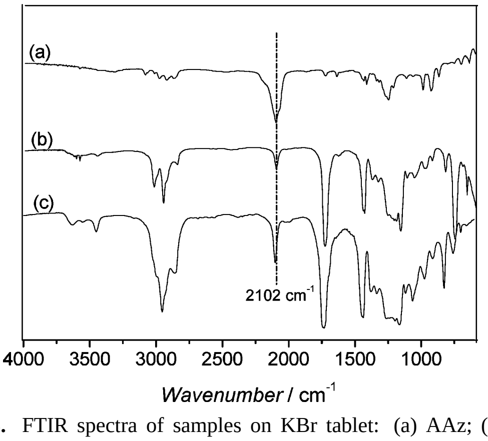

Figure 3. FTIR spectra of samples on KBr tablet: (a) AAz; (b) poly(AAz-*co*-MA) (M_n = 6000, M_w/M_n = 1.15); (c) poly(AAz-*co*-MA) (M_n = 28800, M_w/M_n = 1.07).

The mole fraction of AAz incorporated into polymer chain was calculated according to the elementary analysis for the copolymers. The results are listed in Table 1. As shown, allyl azide can be markedly incorporated into the polymer chain in the polymerization under γ-ray irradiation, and the amount increased with monomer conversion. The results were consistent with those in ATRP and RAFT polymerizations reported by the groups of Sen[26−28] and Klumperman.[29−32] Sen and co-workers reported the synthesis of random copolymers of MA and 1-alkenes resulting in greater than 20% incorporation of the latter in the copolymer.[26] Klumperman and co-workers had demonstrated that allyl monomer could behave as a comonomer, and chain transfer to allyl monomer could almost be negligible in the ATRP copolymerization of MA and 1-octene.[29] For this study, it is clear that there is no peaks corresponding to double bond of allyl azide in ^{1}H NMR spectrum of poly(AAz-*co*-MA) (see Supporting Information), which indicates that allyl azide can mainly act as a comonomer in the polymerization at 0 °C under γ-ray irradiation.

One of our major concerns regarding the polymerizations is the stability of azido group under ^{60}Co γ-ray irradiation. Yang and Shen[33] reported that allyl azide could react with alkenes carrying elecron-withdrawing groups to give 2,3,7-triaza-bicyclo-[3,3,0]-oct-2-ene or its isomer at 20 °C. In this study, to clarify the point, the resultant copolymers (entries 1 and 3, Table 1) and monomer (AAz) were characterized by FTIR spectra (Figure 3). From the figure, it could be

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(23) Bai, R. K.; You, Y. Z.; Pan, C. Y. *Macromol. Rapid Commun.* **2001**, *22*, 315−319.

(24) He, T.; Zheng, G. H.; Pan, C. Y. *Macromolecules* **2003**, *36*, 5960−5966.

(25) Hua, D. B.; Xiao, J. P.; Bai, R. K.; Lu, W. Q.; Pan, C. Y. *Macromol. Chem. Phys.* **2004**, *205*, 1793−1799.

(26) Liu, S. S.; Elyashiv, S.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 12738−12739.

(27) Liu, S. S.; Sen, A. *J. Polym. Sci. Part A, Polym. Chem.* **2004**, *42*, 6175−6192.

(28) Liu, S.; Gu, B.; Rowlands, H. A.; Sen, A. *Macromolecules* **2004**, *37*, 7924−7929.

(29) Venkatesh, R.; Harrisson, S.; Haddleton, D. M.; Klumperman, B. *Macromolecules* **2004**, *37*, 4406−4416.

(30) Venkatesh, R.; Klumperman, B. *Macromolecules* **2004**, *37*, 1226−1233.

(31) Venkatesh, R.; Staal, B. B. P.; Klumperman, B. *Chem. Commun.* **2004**, 1554−1555.

(32) Venkatesh, R.; Vergouwen, F.; Klumperman, B. *J. Polym. Sci. Part A, Polym. Chem.* **2004**, *42*, 3271−3284.

(33) Yang, C. H.; Shen, H. J. *Tetrahedron Lett.* **1993**, *34* (25), 4051−4054.

clearly seen that the peak at 2102 cm^{-1} arisen from -N_3 has remained unchanged between the monomer and the copolymers. The result indicated that azido group was stable at 0 °C throughout the γ-ray radiation process.

In summary, controlled/living free radical polymerization of allyl azide was achieved under ^{60}Co γ-ray irradiation at 0 °C in the presence of BPDTC. The results indicated that allyl azide could be markedly incorporated as a comonomer into the polymer chain in the polymerization under γ-ray irradiation. FTIR spectra of the copolymers showed azido group was stable under γ-ray irradiation. To our knowledge, this is the first report for azide polymer to be synthesized by controlled/living free radical polymerization. This work indicates that polymerization initiated by γ-ray can be a strategy to synthesize azide polymers with controlled molecular weight such as random copolymers, block copolymers, and star-shaped polymers. Further extensive work is underway in our lab.

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Supporting Information Available: Synthesis of allyl azide, polymerization, ^1H NMR spectra of allyl azide and poly(AAz-*co*-MA), FTIR spectra of poly(AAz-*co*-St) and poly(AAz-*co*-MMA). This material is available free of charge via the Internet at http://pubs.acs.org.

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