

Optimization of Atom Transfer Radical Copolymerization of Allyl Butyl Ether with Acrylonitrile

A. S. BRAR[†] and Tripta SAINI

Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi-110016, India

(Received November 13, 2006; Accepted March 8, 2007; Published April 27, 2007)

ABSTRACT: The optimization of atom transfer radical polymerization (ATRP) conditions for the copolymerization of allyl butyl ether with acrylonitrile has been carried out with the aim of achieving control over molecular parameters. The influence of solvents, initiator concentration and in-feed molar compositions on the rate of copolymerization was also investigated. The molecular weight data as well as kinetic studies suggested conventional ATRP behavior of the copolymerization of acrylonitrile and allyl butyl ether. The variation of copolymer composition (F_C) with conversion indicated towards the synthesis of copolymers having significant changes in composition with conversion. The copolymer compositions obtained from ^1H NMR spectra were utilized to determine the reactivity ratios. With the help of DEPT (Distortionless Enhancement by Polarization Transfer) and 2D HSQC (Heteronuclear Single Quantum Coherence) NMR spectra, complete spectral assignments of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were done. All these analysis, considered in aggregate indicated that allyl butyl ether acted as a comonomer instead of a chain-transfer agent under the employed reaction conditions. [doi:10.1295/polymj.PJ2006160]

KEY WORDS Atom Transfer Radical Polymerization (ATRP) / Gel Permeation Chromatography (GPC) / Kinetics / Molecular Weight Distribution / NMR /

The homopolymerization of allyl butyl ether, being an allylic monomer is very unlikely from the free-radical perspective and if it does occur, it polymerizes at rather low rates resulting in very low molecular weight products.¹ This effect is the consequence of degradative chain transfer, in which the propagating radical is very reactive whereas the allylic C–H bond in the monomer is quite weak. As a result, facile chain transfer to monomer occurs (Scheme 1). The weakness of the allylic C–H bond arises from the high resonance stability of the allylic radical that is formed. This allylic radical is too stable to reinitiate polymerization and undergoes termination by reaction with another allylic radical or, more likely, with propagating radicals.²

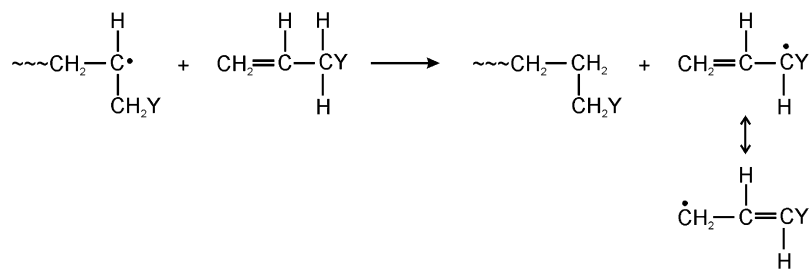
Irrespective of the problems encountered in the homopolymerization of allyl ethers, their copolymers are formed relatively more readily. The copolymers based on allyl butyl ether are useful in a variety of end-use areas¹ such as coatings, adhesives, elastomers, and thickening agents. The incorporation of very small quantities of the allyl monomer gives substantial improvements in the physical properties such as tensile strength, modulus, crush resistance etc. Despite these applications and others that could be developed by structural control, less attention has been paid to the synthesis of polymers containing allyl butyl ether by controlled radical polymerization (CRP). Various CRP techniques^{3–14} provide control over the macromolecular structures, particularly, the molecular

weight distribution, composition and architecture. In recent years, CRP techniques have been employed for the (co)polymerization of monomers that has previously been considered unlikely to polymerize *via* a radical mechanism.^{15–24}

Among different CRP techniques, atom transfer radical polymerization (ATRP)^{25–31} has rapidly attracted growing interest because of the versatility in the synthesis of polymers with predetermined molecular weights, low polydispersities, functionalities, and therefore, specific properties. Recently, ATRP has been used successfully for the synthesis of copolymers of allyl butyl ether with acrylates (methyl acrylate, *n*-butyl acrylate)³² and the characterization of the resulting copolymers was done using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). To the best of our knowledge, no attempts have been made so far for the well-controlled synthesis of copolymers of allyl butyl ether with acrylonitrile.

In this article, the detailed study of copolymerization of allyl butyl ether with acrylonitrile, using ATRP technique is presented for the first time. The optimization of various reaction conditions was done in order to achieve copolymers of predetermined molecular weight and narrow molecular weight distribution. Detailed investigation of reaction kinetics as well as molecular weight distribution data was done to check the controllability of ATRP process. In order to maintain the homogeneity of the reaction mixture, the

[†]To whom correspondence should be addressed (Tel: +91-11-26591377, Fax: +91-11-25195693, E-mail: asbrar@chemistry.iitd.ernet.in).



Scheme 1. Representation of degradative chain transfer in allyl monomers.

polymerization was carried out using different solvents. Further the effects of the monomer feed composition and the influence of allyl butyl ether on the copolymerization were investigated. The detailed NMR analysis of these copolymers was done with the aid of DEPT (Distortionless Enhancement by Polarization Transfer) and 2D HSQC (Heteronuclear Single Quantum Coherence) NMR spectra to confirm the incorporation of allyl butyl ether in the copolymer chains.

EXPERIMENTAL

Materials

Allyl butyl ether (C) (Aldrich, 98%) and acrylonitrile (A) (CDH, 99%) were passed through alumina column to remove inhibitor, vacuum distilled and kept below 5 °C prior to use. 2-Bromopropionitrile (BPN) (Aldrich, 97%), *N,N,N',N',N''*-pentamethyldiethylene-triamine (PMDETA) (Aldrich, 99%), ethylene carbonate (Aldrich, 98%), 1,4-dimethoxybenzene (*p*-dmb) (Aldrich, 99%) and copper bromide (CuBr) (Aldrich, 99.99%) were used as received. 2,2'-bipyridine (bpy) (CDH, 99.5%) was recrystallized from acetone dried in vacuum before use. The solvents toluene (Merck, 99%) and *p*-xylene (CDH, 98.5%) were dried on sodium and distilled before use.

Polymerization

The copolymerization of allyl butyl ether (C) and acrylonitrile (A) was carried out under ATRP conditions using BPN as an initiator at 60 °C. The copolymerization was attempted in bulk as well as in different solvents (25% v/v) (toluene, *p*-xylene, 1,4-dimethoxybenzene). The molar ratio for polymerization were taken as [Monomers]₀: [BPN]₀: [CuBr]₀: [bpy]₀ = 100:1:0.5:1.5. The polymerizations were performed using standard Schlenk line techniques under a nitrogen atmosphere. In a typical procedure, calculated amount of the monomers, ligand along with copper bromide was taken in a round bottom flask; the contents were then degassed by three vacuum-nitrogen cycles and stirred for 10 min. Calculated amount of purged initiator was then added to the reaction flask which was then placed in an oil bath maintained at

60 °C after sealing with septum. The progress of the polymerization was monitored by taking out small aliquots from the reaction flask at timed intervals, yielding copolymer samples at different degrees of conversion. The aliquots, after dilution with tetrahydrofuran (THF), were passed through a neutral alumina column to remove the catalyst. The excess THF was removed by rotary evaporation and the polymer was precipitated in large excess of methanol/water (1:1) system. The precipitated polymer was dried in a vacuum oven at 30 °C until constant weight was reached.

Characterization

The monomer conversion was determined gravimetrically. The molecular weight (M_n) and the polydispersity index (M_w/M_n) (PDI) were measured using Gel Permeation Chromatography (GPC) equipped with a Waters 501 pump with guard column and a Waters 410 RI detector against polystyrene standards. The HPLC grade tetrahydrofuran (THF) was used as eluent at the flow rate of 0.5 mL/min at room temperature. ¹H NMR spectra was utilized to determine the copolymer composition of all the polymer samples withdrawn at different conversions for each in-feed molar ratio. All the NMR measurements (¹H, ¹³C{¹H}, DEPT, HSQC) were done at 25 °C on about 10% polymer solutions in CDCl₃ using Bruker DPX-300 spectrometer operating at 300.15 MHz for ¹H and at 75.5 MHz for ¹³C nuclei using standard pulse sequences as reported in our earlier publications.³³ The signal intensities of the spectra peaks were measured from the integrated peak areas calculated with an electronic integrator.

RESULTS AND DISCUSSION

In order to obtain well-defined copolymers, it is essential to optimize the experimental reaction conditions according to those employed for the corresponding homopolymers. The homopolymerization of acrylonitrile (A) was performed under the optimized reaction conditions using 2-bromopropionitrile (BPN) as an initiator and CuBr/2,2'-bipyridine (bpy) as the catalyst.^{34,35} Under similar conditions, homo-

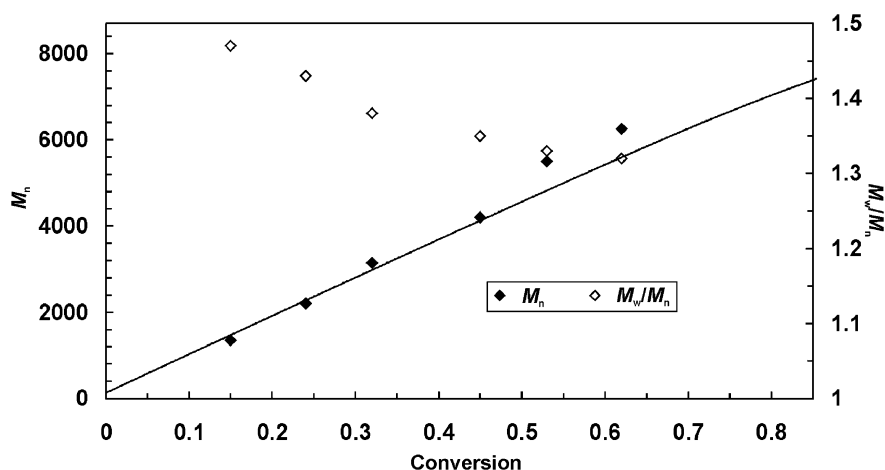


Figure 1. Evolution of M_n and M_w/M_n with conversion for the bulk copolymerization of A/C at 60°C. $[A]_0:[C]_0:[BPN]_0:[CuBr]_0:[bpy]_0 = 60:40:1:0.5:1.5$. Solid lines indicate the theoretical number-average molecular weights, $M_{n,th}$.

polymerization of allyl butyl ether (C) was attempted which does not yield any polymer even after a long reaction time. The failure of this experiment can be attributed to variety of factors like the lack of activating groups (such as esters and aryl groups) in the monomer, allyl butyl ether and the allylic nature of allyl butyl ether. The allylic monomers undergo degradative chain transfer to allylic hydrogens; the stable allylic radical thus derived from monomer is slow to reinitiate and more prone to terminate. However, it has been reported that despite the problems encountered in the homopolymerization of allylic monomers, their copolymerization with other monomers proceeds with less difficulty.¹

Keeping all these points in mind, the initial experiment was carried out using BPN as initiator and CuBr/*N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as catalyst with the molar ratio $[A]_0:[C]_0:[BPN]_0:[CuBr]_0:[PMDETA]_0 = 60:40:1:0.5:0.5$. The reaction mixture, initially blue in color, soon turned heterogeneous (after 15–20 min) due to the formation of dark green colored precipitate sticking to the sides of the reaction flask. However, despite the slow rate, the polymerization does happen, reaching about 8% conversion after 48 h. Moving further in this direction, another test reaction was performed, but this time with bpy as the ligand. Under these conditions, the polymerization was homogeneous in the beginning and proceeded at a reasonable rate, reaching about 30% conversion in 6 h.

The evolution of molecular weight and molecular weight distribution as a function of monomer conversion are displayed in Figure 1. Molecular weights of the A/C copolymers, experimentally determined by GPC, showed linear variation with monomer conversion. At the same time, relatively narrow polydispersities were obtained ($1.3 < M_w/M_n < 1.5$), indicat-

ing towards successful employment of ATRP for the synthesis of A/C copolymers. The variation of molecular weight showed satisfactory agreement between the theoretical and experimental values. However, $M_{n,GPC}$ were slightly higher than the theoretical values for conversion beyond $\sim 45\%$ conversion, which could be due to the insolubility of the deactivator species in the reaction media. Figure 2 shows the first-order kinetic plot of A/C copolymerization conducted under bulk conditions using bpy as the catalyst. It showed that $\ln[M]_0/[M]$ increased with time and at short times corresponding to low conversions, does so in a linear fashion. However as the reaction time increased (beyond 45% conversion) some curvature began to occur, which again indicate towards the loss of control beyond 45% conversion. One probable reason behind this could be the heterogeneity observed at higher conversions due to the insoluble deactivator species.

In order to maintain the homogeneity of the system, the polymerization was attempted in different solvents. The choice of solvent was made on the basis of increased solubility of the reaction contents in the solvent. Ethylene carbonate, despite showing good results for the synthesis of acrylonitrile polymers of well-defined molecular parameters, could not be used in this case due to the insolubility of allyl butyl ether in this solvent. The polymerization was then attempted in toluene, *p*-xylene and *p*-dimethoxybenzene (*p*-dmb). The trend of number-average molecular weight (M_n) and polydispersity (M_w/M_n) with the conversion for A/C copolymerization in three different solvents is displayed in Figure 3. Almost similar results are obtained for these three solvents. The evolution of M_n , and M_w/M_n with conversion for the A/C copolymerization in different solvents was investigated and the linear variation indicated that the concen-

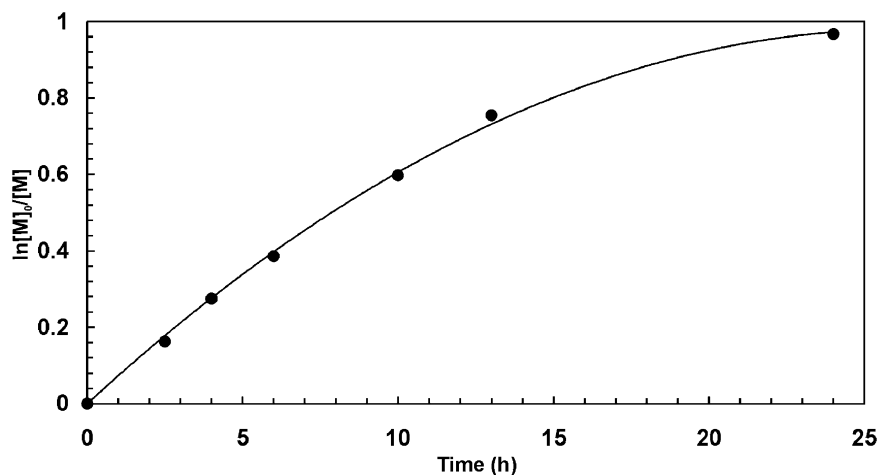


Figure 2. Variation of $\ln[M]_0/[M]$ with the reaction time for the bulk copolymerization of A/C at 60 °C. $[A]_0:[C]_0:[BPN]_0:[CuBr]_0:[bpy]_0 = 60:40:1:0.5:1.5$.

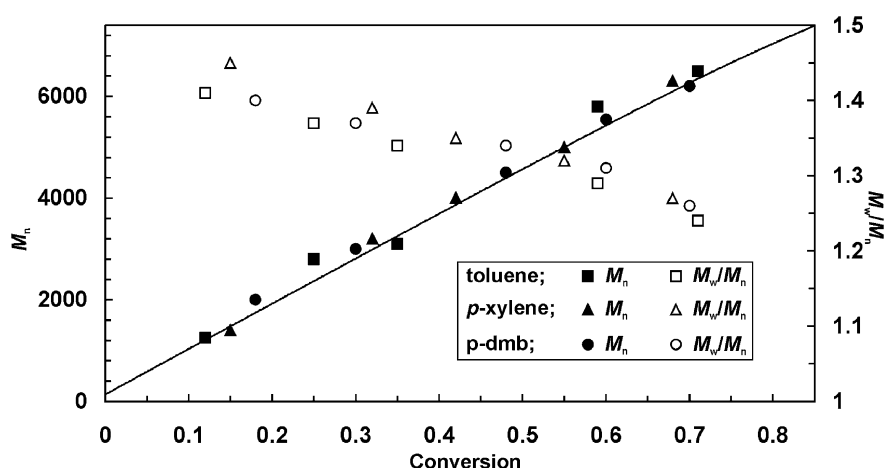


Figure 3. Dependence of molecular weights and polydispersities with conversion for the ATRP of A/C at 60 °C in three different solvents. $[A]_0:[C]_0:[BPN]_0:[CuBr]_0:[bpy]_0 = 60:40:1:0.5:1.5$. Solid lines indicate the theoretical number-average molecular weights, $M_{n,th}$.

tration of growing radical is constant with negligible contribution from termination reactions.

The polymerization proceeded at a relatively slow rate; the results are summarized in Table I. Though, the results for solution polymerization of A/C copolymers showed better control than that in bulk, yet the heterogeneity was not completely removed with the use of solvents as well. Hence in order to obtain well-controlled ATRP of A/C, the polymerization was not continued beyond 65–70% monomer conversion, until the point till the polymerization mixture retained homogeneity. For further optimization, toluene was chosen as a solvent on an arbitrary basis.

Effect of Initiator Concentration

Figure 4 shows the kinetic plots of $\ln[M]_0/[M]$ vs time for the ATRP of A/C catalyzed by CuBr/bpy in toluene and initiated by BPN at various initiator concentrations. The polymerizations were approximately first-order with respect to the monomer. The

Table I. Percent monomer conversion for the copolymerization of A/C at 60 °C in three different solvents. $[A]_0:[C]_0:[BPN]_0:[CuBr]_0:[bpy]_0 = 60:40:1:0.5:1.5$

No.	toluene		<i>p</i> -xylene		<i>p</i> -dmb	
	Conv (%)	Time (h)	Conv (%)	Time (h)	Conv (%)	Time (h)
1	12	4.0	15	5.0	18	4.5
2	25	7.5	32	10.0	30	9.0
3	35	11.8	42	15.0	48	16.0
4	59	22.0	55	20.0	60	24.0
5	71	30.0	68	28.0	70	29.0

slopes of the kinetic plots revealed that the concentration of active species remained constant throughout the polymerization. Results from kinetic studies for three different initiator concentration showed that the rate of polymerization is first order with respect to the initiator. With the increase in the initial concentration of initiator, the polymerization proceeded at a

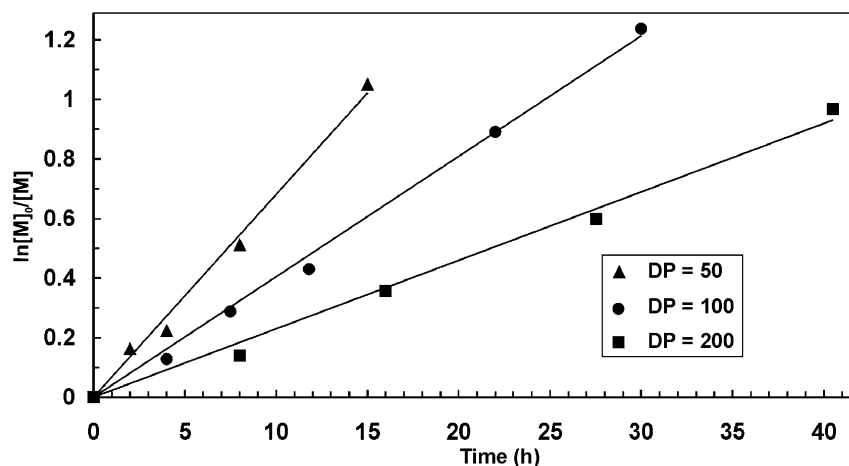


Figure 4. Plots of $\ln[M]_0/[M]$ versus reaction time for the ATRP of A/C at 60 °C using CuBr/bpy at different $[BPN]_0$. ($[Monomers]_0/[BPN]_0 = 50/1; 100/1; 200/1$).

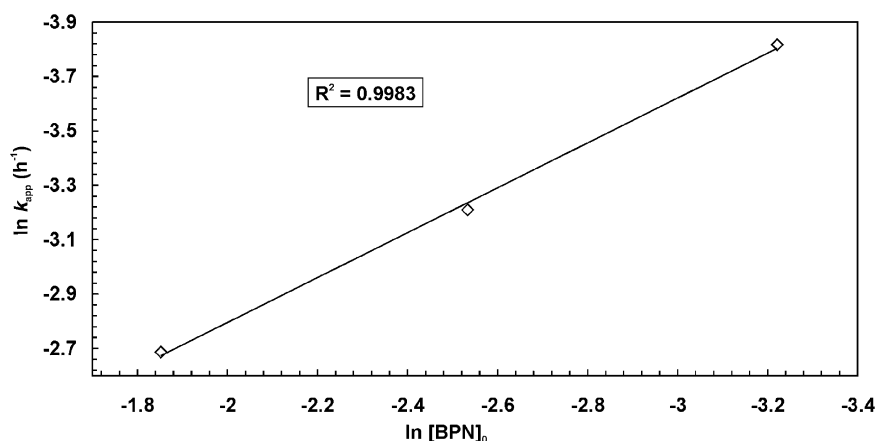


Figure 5. Dependence of k_{app} on $[BPN]_0$. ($[Monomers]_0/[BPN]_0 = 50/1; 100/1; 200/1$).

faster rate. The dependence of the apparent rate of polymerization (k_{app}) on the concentration of initiator was elucidated by plotting $\ln k_{app}$ against $\ln[BPN]_0$ as shown in Figure 5. The slope of the line indicated an apparent 0.83 order with respect to the initiator in this system.

In order to confirm the controllability of ATRP process, molecular weight distribution was investigated with conversion. The data is shown in Figure 6. The molecular weights varied linearly with conversion while maintaining low polydispersities. Good agreement between the experimental and the theoretical M_n values indicate towards the good initiating efficiency ($f = M_{n,theo}/M_{n,GPC}$) of the initiator, 2-bromopropionitrile (BPN) for the atom transfer radical copolymerization of acrylonitrile/allyl butyl ether.

For polymerizations in toluene as solvent, the molecular weight data (linear variation of M_n with conversion with relatively low polydispersities) as well as kinetic studies (linear first order kinetic plot) suggests that the copolymerization proceeds through con-

ventional ATRP behavior that is no peculiarities were caused by the incorporation of allyl butyl ether in the polymer chains.

Effect of Variation of In-Feed Molar Composition

To study the variation of copolymer composition during the progress of polymerization, the A/C copolymers were synthesized at 60 °C in toluene with BPN as initiator and CuBr/bpy catalyst, by varying the in-feed molar ratios; the results are summarized in Table II. As the fraction of allyl butyl ether was increased in the monomer feed, its incorporation was found to be higher in the copolymer. However, the higher fraction of allyl butyl ether in the monomer feed resulted in a lower overall monomer conversion in conjunction with a lower molar mass.

The reason behind this also lies in the allylic nature of the monomer. As allyl butyl ether does not homopolymerize, when most of the acrylonitrile was consumed, there was not enough acrylonitrile remaining for allyl butyl ether to cross-propagate. The C unit ter-

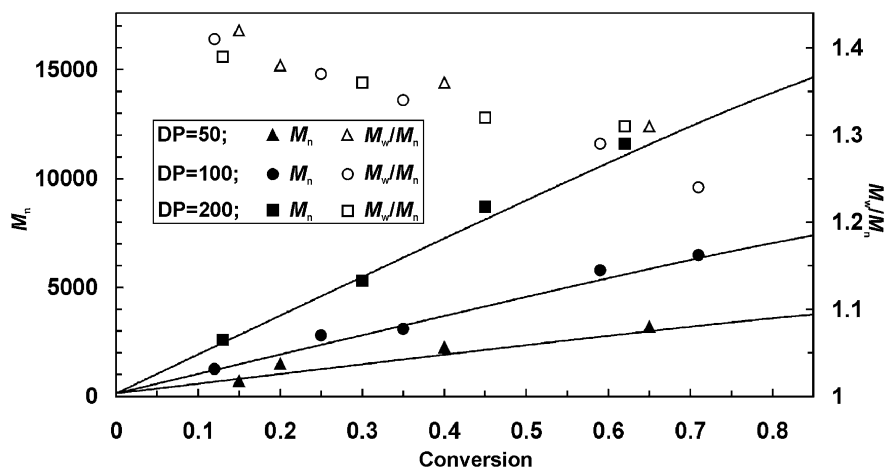


Figure 6. Evolution of M_n and M_w/M_n with conversion for ATRP of A/C at 60°C using CuBr/bpy at different $[BPN]_0$. ($[Monomers]_0/[BPN]_0 = 50/1; 100/1; 200/1$). The solid line is for simulated M_n based on $[Monomers]_0$ and $[BPN]_0$.

Table II. ATRP of A/C at 60°C in toluene with BPN as initiator and CuBr/bpy catalyst system for different monomer feed conditions (f_C) $[A+C]_0:[BPN]_0:[CuBr]_0:[bpy]_0 = 100:1:0.5:1.5$

No.	f_C (in-feed molar fraction)	F_C (outfeed molar fraction)	Overall Conversion (%)	M_n	M_w/M_n
1	0.40	0.20	71	6500	1.24
2	0.60	0.30	50	4800	1.27

minated by halogen atom can be slowly activated leading to the formation of C radical. Hence, during the initial stages of polymerization, when excess of A unit is present in the reaction media, cross-propagation occurs at a faster rate, *i.e.*, C radical propagates by addition to A unit and polymer chains grow in controlled manner yielding polymers having expected molecular weights and low polydispersities. However, when most of A unit is consumed and concentration of C monomer unit is higher in the reaction media (*i.e.*, for high conversions), then there are more chances of interaction of C radical with C monomer unit. The C monomer, being allylic in nature undergoes degradative chain transfer to allylic hydrogens as shown in Scheme 1. The allylic radical thus generated is very stable and hence very slow to reinitiate and is more prone to terminate. Due to this, polymerization is limited to low conversions only. Thus, increasing the fraction of allyl butyl ether in the monomer feed reduced the overall conversion.

Copolymer Composition and Reactivity Ratio Determination

The copolymer compositions were determined from the 1H NMR spectra by correlating the relative intensities of the signals of the methyl ($-CH_3$) protons in

the allyl butyl ether (C) unit and rest of the protons in the A+C unit.

For polymerizations involving high conversions, accurate values of reactivity ratios are not obtained using low conversion methods.^{36,37} Hence, the reactivity ratios were optimized using the least square methodology described elsewhere.³⁸ The theoretical outfeeds at high conversions were calculated by following the model proposed by Heatley *et al.*³⁹ and Mao and Huglin⁴⁰ and optimization was done as described earlier.⁴¹ The optimized reactivity ratios were found to be $r_A = 6.01$ and $r_C = 0.10$, revealing the lower reactivity of allyl butyl ether for the copolymerization.

Due to large difference in the monomer reactivity ratios, any variation in the relative concentration of monomers may incorporate gradiency^{42–44} in the copolymer chains. Figure 7 shows F_C (molar fraction of C unit in the copolymer) as a function of the conversion for two different in-feed compositions (f_C). The variation of F_C with the conversion indicated the presence of gradiency in the copolymer composition. The experimental values being in good agreement with the theoretical ones reflect the radical nature of the polymerization mechanism.

NMR Analysis

In order to fully characterize the structure of A/C copolymers, detailed NMR analysis was carried out. Figure 8 shows the completely assigned $^{13}C\{^1H\}$ NMR spectrum of A/C copolymer having $F_C = 0.3$. The spectral assignments were done with the help of $^{13}C\{^1H\}$ NMR spectrum of polyacrylonitrile and DEPT NMR spectrum of A/C copolymer. The spectral region from 117–124 ppm was assigned to the nitrile carbon from A unit. The ($^4CH_2 + ^5CH_2$) carbons of the C unit appeared in the spectral region 69–75 ppm.

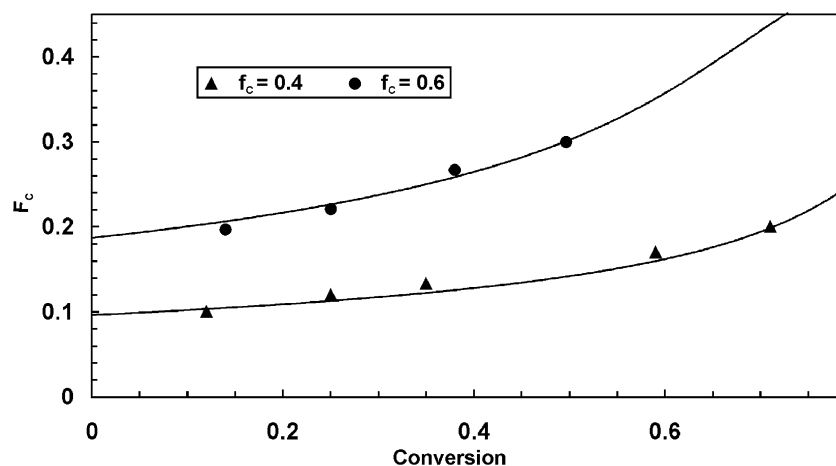


Figure 7. Variation of copolymer composition (F_C) as a function of conversion of A/C copolymers synthesized by ATRP.

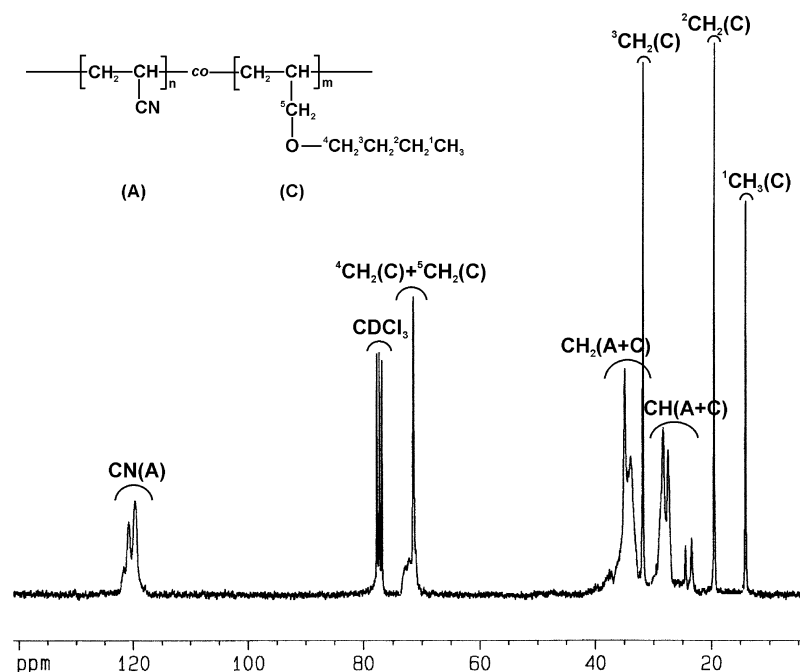


Figure 8. Assigned $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of A/C copolymer synthesized by ATRP having $F_C = 0.30$.

Utilizing carbon-13 DEPT-135 NMR spectrum (Figure 9a), the complex and overlapping resonances in the spectral region 31–38 ppm were assigned to the backbone methylene carbons from both A and C unit. The signals at 31.7 ppm, 19.5 ppm, and 14.5 ppm were ascribed to $^3\text{CH}_2$, $^2\text{CH}_2$, and $^1\text{CH}_3$ carbons of C unit, respectively. With the help of carbon-13 DEPT-90 NMR spectrum (Figure 9b), the resonance signals obtained from 22.5–30.0 ppm were assigned to the backbone methine carbons from both A and C units.

With the help of completely assigned $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, regions corresponding to various protons in the 2D HSQC NMR spectra were assigned. 2D HSQC NMR spectrum of A/C copolymer having

$F_C = 0.3$ is shown in Figure 10. It provides information about one bond correlation between ^1H and ^{13}C nuclei. The cross peak 1 was assigned to the ^1H - ^{13}C coupling of $^1\text{CH}_3$. The protons and carbon of $^2\text{CH}_2$ couple to gave cross peak 2. Similarly, ($^4\text{CH}_2 + ^5\text{CH}_2$) showed cross peaks 3 and 4. The ^1H - ^{13}C coupling of the backbone methine and methylene protons corresponds to the region I and II, respectively. Using the information obtained from the assignments made in 2D HSQC NMR spectrum, the ^1H NMR spectrum was assigned completely and is shown in Figure 11.

The complex and overlapping resonances in $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra, different from those expected from the homopolymers, reflects that allyl

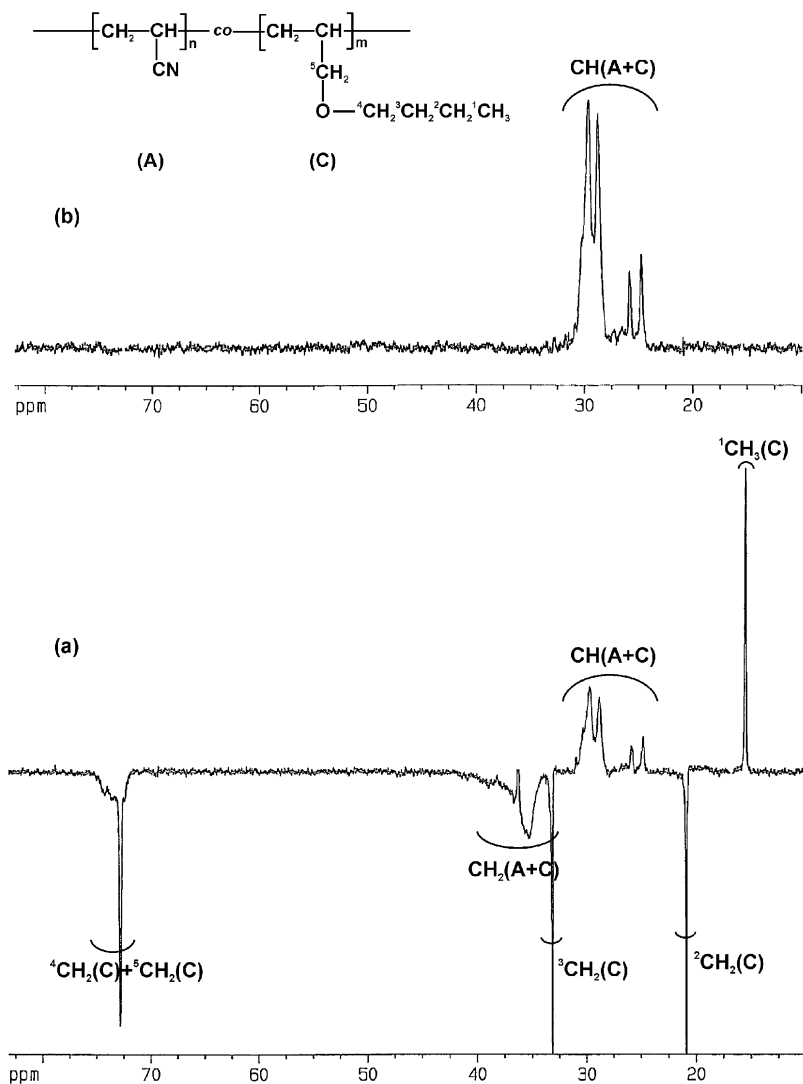


Figure 9. DEPT NMR spectra of A/C copolymer synthesized by ATRP having $F_C = 0.30$ (a) DEPT-135 NMR spectrum and (b) DEPT-90 NMR spectrum.

butyl ether is behaving as a comonomer rather than a chain-transfer agent.

CONCLUSIONS

ATRP of allyl butyl ether with acrylonitrile was investigated. The reaction conditions were optimized in order to obtain A/C copolymers of controlled molecular parameters. Using 2-bromopropionitrile as initiator and CuBr/bpy as catalyst, well-defined copolymers having about 30 mol % allyl butyl ether were obtained. The solution polymerization provide better control than the bulk copolymerization, however, the heterogeneity was not completely eliminated. The molecular weights as high as 11000 and narrow molecular weight distribution were obtained for polymerization in toluene; suggested conventional ATRP behavior. Increasing the fraction of allyl butyl ether in the monomer feed led to an increase in the level of incor-

poration of allyl butyl ether in the copolymer at the expense of the overall conversion. The optimized reactivity ratios were found to be $r_A = 6.01$ and $r_C = 0.10$, which reflect the lower reactivity of allyl butyl ether for the copolymerization with acrylonitrile. The complex and overlapping ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were resolved completely using DEPT and 2D HSQC NMR spectra. ATRP resulted in a significant incorporation of allyl butyl ether within the copolymer chains along with excellent control of the polymerizations; this fact clearly indicates that allyl butyl ether acted as a comonomer rather than a chain-transfer agent under the employed reaction conditions.

Acknowledgment. One of the authors (Tripta Saini) thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India for providing the financial support.

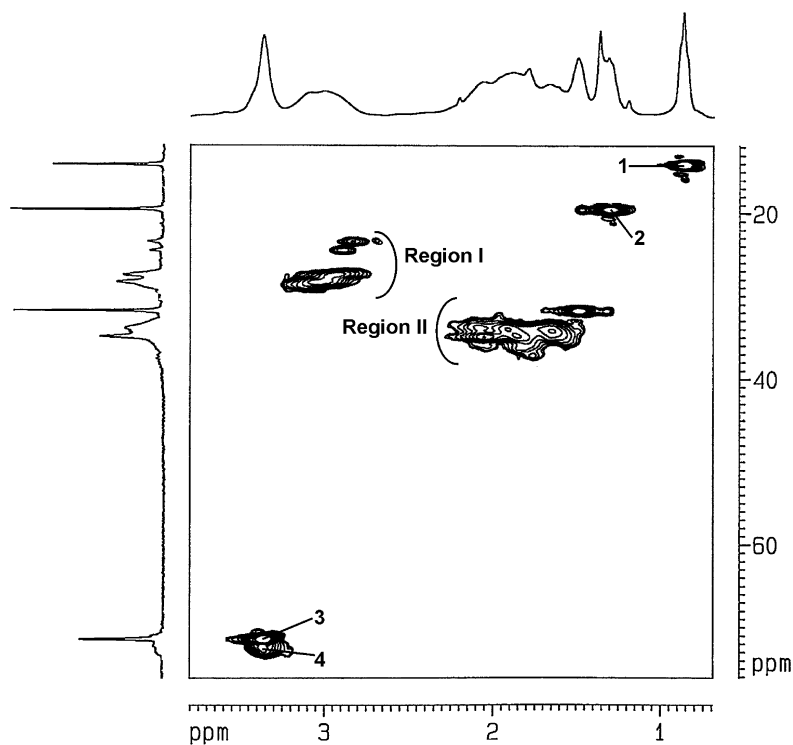


Figure 10. 2D HSQC NMR spectrum of A/C copolymer having $F_C = 0.30$.

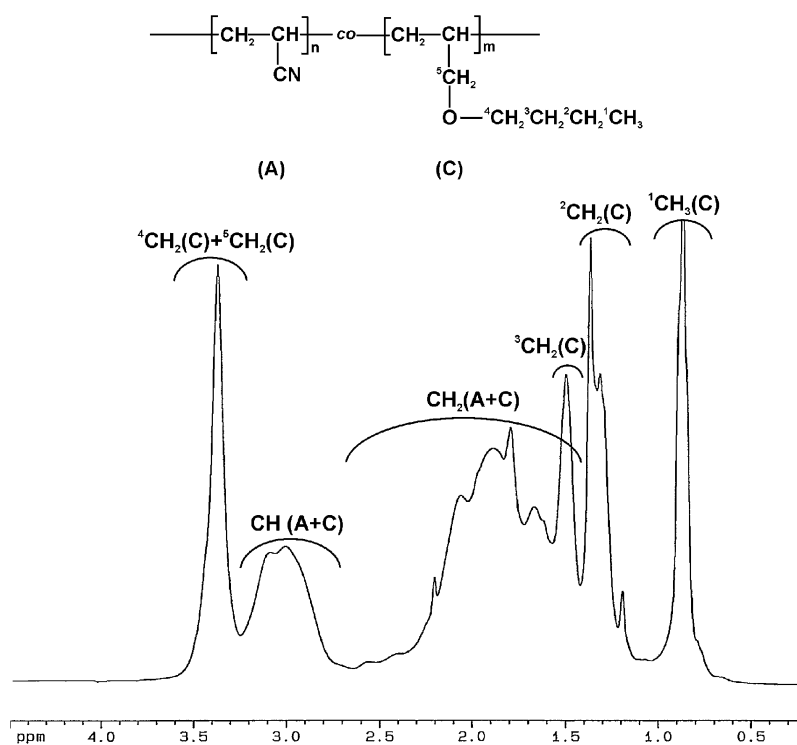


Figure 11. The ^1H NMR spectrum of A/C copolymer having $F_C = 0.30$.

REFERENCES

1. J. J. J. Cahill, in "Encyclopedia of Polymer Science and Engineering," Vol 1, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Ed., Wiley, New York, 1964, p771.
2. G. Odian, "Principles of Polymerization," John Wiley & Sons Inc, New York, 1991, p266.
3. "Advances in Controlled/Living Radical Polymerization," ACS Symposium Series 854, K. Matyjaszewski, Ed., Am. Chem. Soc., Washington DC, 2003.
4. A. Goto and T. Fukuda, *Prog. Polym. Sci.*, **29**, 329 (2004).
5. K. Matyjaszewski and J. Xia, *Chem. Rev.*, **101**, 2921 (2001).
6. M. Sawamoto, M. Kamigaito, and T. Ando, *Chem. Rev.*,

- 101, 3689 (2001).
7. M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rec.*, **4**, 159 (2004).
 8. C. J. Hawker, A. W. Bosman, and E. Harth, *Chem. Rev.*, **101**, 3661 (2001).
 9. D. H. Solomon, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 5748 (2005).
 10. A. Studer and T. Schulte, *Chem. Rec.*, **5**, 27 (2005).
 11. C. Barner-Kowollik, T. P. Davis, J. P. A. Heuts, M. H. Stenzel, P. Vana, and M. J. Whittakar, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 365 (2003).
 12. S. Perrier and P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 5347 (2005).
 13. J. Qiu, T. Pintauer, S. G. Gaynor, K. Matyjaszewski, B. Charleux, and J. P. Vairon, *Macromolecules*, **33**, 7310 (2000).
 14. B. K. Denizli, J. F. Lutz, L. Okrasa, T. Pakula, A. Guner, and K. Matyjaszewski, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 3440 (2005).
 15. R. Venkatesh and B. Klumperman, *Macromolecules*, **37**, 1226 (2004).
 16. N. K. Singha, B. Ruitter, and U. S. Schubert, *Macromolecules*, **38**, 3596 (2005).
 17. J. Huang and K. Matyjaszewski, *Macromolecules*, **38**, 3577 (2005).
 18. R. Paris and J. L. de la Fuente, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2395 (2005).
 19. G. Masci, D. Bontempo, N. Tiso, M. Diociaiuti, L. Mannina, D. Capitani, and V. Crescenzi, *Macromolecules*, **37**, 4464 (2004).
 20. Q. Smith, J. Huang, K. Matyjaszewski, and Y. L. Loo, *Macromolecules*, **38**, 5581 (2005).
 21. A. S. Brar and S. Kaur, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 1745 (2006).
 22. R. M. Kris, Vidts, and Filip E Du Prez., *Eur. Polym. J.*, **42**, 43 (2006).
 23. S. Liu, S. Elyashiv, and A. Sen, *J. Am. Chem. Soc.*, **123**, 12738 (2001).
 24. M. S. Donovan, A. B. Lowe, T. A. Sanford, and C. L. McCormick, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 1262 (2003).
 25. V. Coessens, T. Pintauer, and K. Matyjaszewski, *Prog. Polym. Sci.*, **26**, 337 (2001).
 26. A. Limer, A. Heming, I. Shirley, and D. Haddleton, *Eur. Polym. J.*, **41**, 805 (2005).
 27. T. Pintauer and K. Matyjaszewski, *Coordination Chem. Rev.*, **249**, 1155 (2005).
 28. J. F. Lutz, H. G. Boerner, and K. Weichenhan, *Macromol. Rapid Commun.*, **26**, 514 (2005).
 29. K. Min and K. Matyjaszewski, *Macromolecules*, **38**, 8131 (2005).
 30. J. Xia, N. A. D. Burke, and H. D. H. Stoever, *Macromolecules*, **39**, 2275 (2006).
 31. X. Lou and L. He, *Langmuir*, **22**, 2640 (2006).
 32. R. Venkatesh, F. Vergouwen, and B. Klumperman, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 3271 (2004).
 33. A. S. Brar, G. Singh, and R. Shankar, *J. Mol. Struct.*, **703**, 69 (2004).
 34. K. Matyjaszewski, S. M. Jo, H. J. Paik, and D. A. Shipp, *Macromolecules*, **32**, 6431 (1999).
 35. C. Tang, T. Kowalewski, and K. Matyjaszewski, *Macromolecules*, **36**, 1465 (2003).
 36. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
 37. T. Kelen and F. Tudos, *J. Macromol. Sci. Chem.*, **A9**, 1 (1975).
 38. A. S. Brar, G. Singh, and R. Shankar, *Eur. Polym. J.*, **40**, 2679 (2004).
 39. F. Heatley, G. Yu, C. Booth, and T. G. Blease, *Eur. Polym. J.*, **27**, 573 (1991).
 40. R. Mao and M. B. Huglin, *Polymer*, **34**, 1709 (1993).
 41. A. S. Brar and T. Saini, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 2955 (2006).
 42. A. S. Brar and T. Saini, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 2810 (2005).
 43. A. S. Brar and S. Kaur, *Polym. J.*, **37**, 316 (2005).
 44. A. S. Brar and T. Saini, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 1975 (2006).