Copolymerization of N-Phenyl Citraconimide with Methyl Methacrylate

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Synthesis and characterization of copolymers prepared by N-phenyl citraconimide, N-(*o*/*m*/*p*-chlorophenyl) citraconimide and N-(*p*-tolyl) citraconimide with methyl methacrylate (MMA) by using controlled free radical initiation (ATRP).

Key Words: Copolymers, N-Phenyl citraconimides, Methyl methacrylate.

INTRODUCTION

Block copolymers of methyl methacrylate (MMA) butyl acrylate and methyl acrylate were synthesized using copper based initiators[1]. It was found that poly(methyl methacrylate) (PMMA) macro initiator is able to initiate the ATRP of acrylic monomers. Polyacrylates must have bromide group as end group to act as macro initiator, which in combination with CuCl can be used for polymerization. This allows halogen exchange to occur, thus increasing the relative rate of initiation to propagate and giving a controlled polymerization. Block copolymers of 1,1-dihydroperfluorooctyl methacrylate and methyl methacrylate in environmentally friendly medium (supercritical carbon dioxide) is reported by Xia *et al.*[2].

The ATRP of methyl methacrylate with differently substituted chloro-telechelic poly(ethylene oxide) macro initiator was reported[3,4]. Phenyl substituted macroinitiator gives better control over the polymerization of methyl methacrylate than methyl and hydrogen substituted macroinitiators. Block copolymer of CCl₃-terminated vinylidene fluxoride telomers and methyl methacrylate were synthesized by using CuBr/bipy system with narrow polydispersities (*ca.* 1.1)[5]. The synthesis of poly(ethylene-co-butylene)-b-poly(methyl methacrylate) *via* ATRP of methyl methacrylate onto a poly (ethylene-co butylene) macro initiator) using CuBr or CuCl or CuSCN/N-penthyl-2-pyridylmethanimine catalytic system was reported by Schellekens *et al.*[6]. The rate of activation of the macro-initiator was strongly affected by the copper counter ion and increases in the order CuSCN < CuBr < CuCl. Other related articles are well documented in the literature[6-10].

Main focus of present work was to investigate synthesis and characterization of N-phenyl citraconimide, N-(*o*/*m*/*p*-chlorophenyl) citraconimide and N-(*p*-tolyl) citraconimide copolymers with methyl methacrylate by using controlled free radical initiation (ATRP).

EXPERIMENTAL

Methyl methacrylate, initiator (Mixture of AIBN, FeCl₃·6H₂O and PPh₃ in the ratio of 1:4:10), argon gas, N-aryl citraconimide, toluene, THF, heptane, CuBr, bipyridine, methanol.

Procedure

Preparation of copolymers using AIBN/FeCl₃·6H₂O/PPh₃: Bulk polymerization of methyl methacrylate (MMA) was carried out in a Schlenck tube using AIBN/FeCl₃·6H₂O/PPh₃ initiator in 1:4:10 molar ratios. A mixture of AIBN (3.02 × 10⁻² mol L⁻¹), FeCl₃·6H₂O (12.0 × 10⁻² mol L⁻¹) and PPh₃ (36.5 × 10⁻² mol L⁻¹) were introduced into Schlenck tube fitted with a three-way stopcock. Three cycle of vacuum/argon were applied in order to remove oxygen. Methyl methacrylate (MMA) (9.30 mol L⁻¹) was added under argon in the tube with a syringe and then the tube was placed in an oil bath at 80 ℃. The mixture was stirred at 80 ℃ for 8 h. After > 95 % conversion, second monomer *i.e.* N-aryl citraconimide dissolved in toluene was added under argon. Toluene solution of the citraconimide monomer was purged thoroughly before adding to the reaction mixture. The reaction mixture was placed in an oil bath at 80 ℃ and reaction was carried out for different time intervals. The resulted polymer was dissolved in THF and precipitated in heptane, finally washed with methanol. The polymer was dried in a vacuum over for 48 h at 50 ℃.

Preparation of copolymers using RX/CuBr/Bpy: Bulk polymerization of MMA was carried out in a Schlenck tube using AIBN/FeCl$_3$·6H$_2$O/PPh$_3$ (1:4:10 molar ratio) initiator. A mixture of AIBN (3.02 × 10^{-2} mol/L), FeCl$_3$·6H$_2$O (12.0 × 10^{-2} mol L^{-1}) and PPh$_3$ (36.5 × 10^{-2} mol L^{-1}) were introduced into Schlenck tube fitted with a three-way stopcock. Three cycle of vacuum/argon were applied in order to remove oxygen. Methyl methacrylate (MMA) (9.30 mol L^{-1}) was added under argon in the tube with a syringe and then the tube was placed in an oil bath at 80 ºC for 3 h. The resulted polymer was dissolved in THF and precipitated in heptane. The precipitated polymer was separated by filtration and washed with methanol to remove the unreacted monomers. The polymer was dried in a vacuum oven for 48 h at 50 ºC. The yield of poly(methyl methacrylate) (PMMA) was *ca.* 80 %.

Poly(methyl methacrylate) thus obtained was used as a macroinitiator for the preparation of block copolymers. poly(methyl methacrylate) macroinitiator (1 × 10^{-2} mol L^{-1}), CuBr (1 × 10^{-2} mol L^{-1}), bipyridine (3 × 10^{-2} mol L^{-1}) and N-phenyl citraconimide (3.40 × 10^{-2} mol L^{-1}) were added into Schlenck tube and purged with argon by repeated vacuum/ argon cycles. Toluene was added under argon with the help of a syringe. The reaction mixture was placed in an oil bath at 80 ºC. Polymer obtained was dissolved in THF and precipitated in heptane. The polymer was washed several times with hot methanol in order to remove unreacted monomer and then dried in vacuum oven for 48 h at 50 ºC.

RESULTS AND DISCUSSION

Characterization of block copolymers prepared using AIBN/FeCl$_3$·6H$_2$O/PPh$_3$: Structural characterization of block copolymers obtained by AIBN/FeCl$_3$·6H$_2$O/PPh$_3$ initiating system was done using ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy. The resonance signals due to the -OCH$_3$ protons of the MMA and aromatic protons of N-aryl citraconimides were present at δ = 3.59 ppm and at δ = 7.20-7.50 ppm, respectively in ^{1}H NMR spectrum (Fig. 1). In the ^{13}C [^{1}H] NMR spectrum of copolymers (Fig. 2) signals due to aromatic carbon of N-aryl citraconimides were present in the range of δ =120.0-130.0 ppm. CHN analysis also confirmed the presence of citraconimide monomer in the polymers. Reaction was carried out for different intervals of time *i.e.* 3 days / 6 days / 9 days and the effect of reaction time on copolymer composition was evaluated. The mole fraction of citraconimide from ^{1}H NMR spectra was calculated by taking the ratio of the intensity of signals due to methoxy protons of MMA and aromatic protons of N-aryl citraconimide. Percentage nitrogen content was also used to calculate the mole fraction of N-aryl citraconimides in copolymers. Mole fraction of citraconimide in copolymers was only 0.04 and 0.06 for PTC and C monomers, respectively even after 9 days of reaction. Increase in reaction time from 3 days to 9 days did not have much effect on the copolymer composition in case of PTC monomer whereas in mole fraction of citraconimide was observed in case of C monomer as the reaction time increased from 3 to 9 days. Further increase in the reaction time had no effect on the composition. The results of the mole fractions calculated using CHN analysis and ^{1}H NMR are given in Table-1.
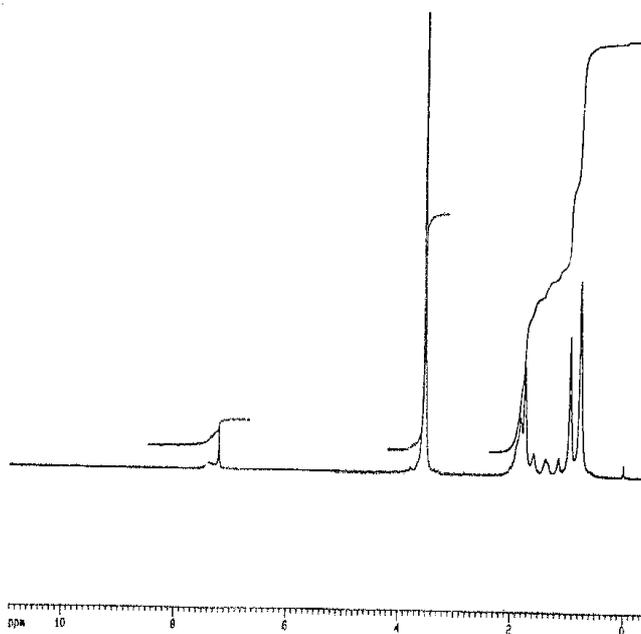

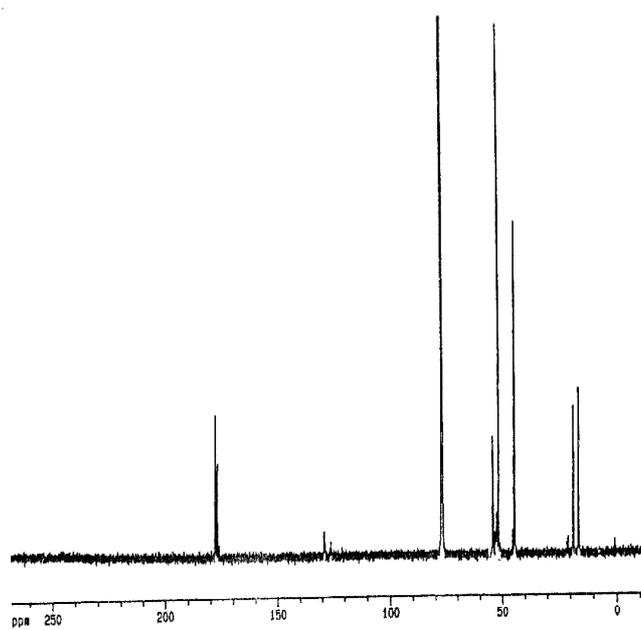Fig. 1. ^{1}H NMR spectra of PMMA-b-PC copolymer prepared by using AIBN/FeCl$_3$·6H$_2$O/PPh$_3$

Fig. 2. ^{13}C{^{1}H} NMR spectra of PMMA-b-PC copolymer prepared by using AIBN/FeCl$_3$·6H$_2$O/PPh$_3$

TABLE-1
MOLE FRACTION OF N-ARYL CITRACONIMIDES IN
COPOLYMERS PREPARED USING AIBN/FeCl$_3$.6H$_2$O/PPh$_3$

S. No.	Monomer*	Time of reaction (days)	Nitrogen (%)	Mole fraction of N-aryl citraconimides in copolymer	
				CHN	^{1}H NMR
1	PTC	3	0.68	0.05	0.04
2	PTC	6	0.65	0.05	0.03
3	PTC	9	0.60	0.05	0.04
4	C	3	0.63	0.05	0.03
5	C	6	0.94	0.07	0.06
6	C	9	0.96	0.07	0.06

*Represent the monomer used for the synthesis of second block (first block is PMMA).

Polymerization for N-(*o*-/*m*-/*p*-chlorophenyl) citraconimides was also carried out under similar condition but no signal due to aromatic protons was detected in ^{1}H NMR.

Characterization of block copolymers prepared using PMMA-Cl /CuBr/Bpy

Poly(methyl methacrylate) (PMMA) macroinitiator: PMMA-Cl macroinitiator obtained by bulk polymerization of MMA using AIBN/FeCl$_3$·6H$_2$O/PPh$_3$ as initiating system was characterized with the help of ^{1}H NMR and ^{13}C {^{1}H} NMR spectroscopic techniques. The resonance signals due to the -OCH$_3$ protons of the MMA was observed at $\delta = 3.59$ ppm. The other characteristic signals of MMA observed at $\delta = 0.80$-1.20 ppm and $\delta = 1.80$-2.00 ppm was due to -CH$_3$ and >CH$_2$, respectively. In ^{13}C{^{1}H} NMR spectrum of PMMA, the resonance signal due to carbonyl carbon was observed at $\delta = 175.0$-178.0 ppm, >CH$_2$ and -OCH$_3$ carbons were observed between $\delta = 52.0$ ppm to $\delta = 55.0$ ppm. Quaternary carbon and -CH$_3$ carbon resonate at $\delta = 44.0$-46.0 ppm and $\delta = 16.0$-20.0 ppm, respectively. Molecular characterization of the polymers was done using GPC and polystyrene as calibration standards, $\overline{M}_n$ and polydispersity index of PMMA was found to be 1.25×10^4 and 1.31, respectively. Calculated molecular weight of PMMA was found to be 1.21×10^4. Thus the observed molecular weight is in good correlation with the calculated value.

Block copolymers: Structural characterization of block copolymers obtained by using PMMA-Cl/CuBr/Bpy initiating system was done by using ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy. ^{1}H NMR spectra of all the block copolymers clearly show the resonance signals due to the -OCH$_3$ protons of MMA and aromatic protons of N-aryl citraconimides at δ 3.59 ppm and $\delta = 7.20$-7.50 ppm, respectively. ^{1}H NMR spectrum of the PMMA-b-PC copolymer is shown in Fig. 3. Signals due to aromatic carbon of N-aryl citraconimides at $\delta = 122$-135 ppm were also percent in ^{13}C{^{1}H} NMR spectra thereby indicating the incorporation of citraconimide monomer in the copolymers. A typical ^{13}C{^{1}H} NMR spectrum of PMMA-b-PC copolymer is shown in Fig. 4. ^{1}H NMR and CHN analysis was used to determine the mole fraction of N-aryl citraconimide in copolymers. The results of mole fraction of citraconimide in copolymer calculated using ^{1}H NMR and elemental analysis are given in Table-2. Only oligomeric blocks of N-aryl citraconimides could be incorporated.

Unimodal curve for all PMMA-b-Poly (N-aryl citraconimide) copolymers were obtained in GPC. Mn and polydispersity index (PDI) in copolymers were calculated and it was found that there is an increase in molecular weight for
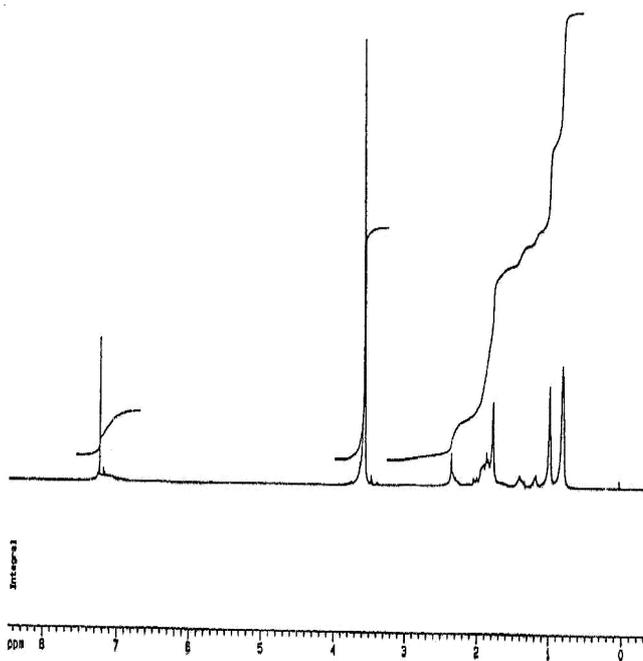

Fig. 3. ^{1}H NMR spectra of PMMA-b-PC copolymer prepared by using PMMA-Cl/CuBr/Bipyridine
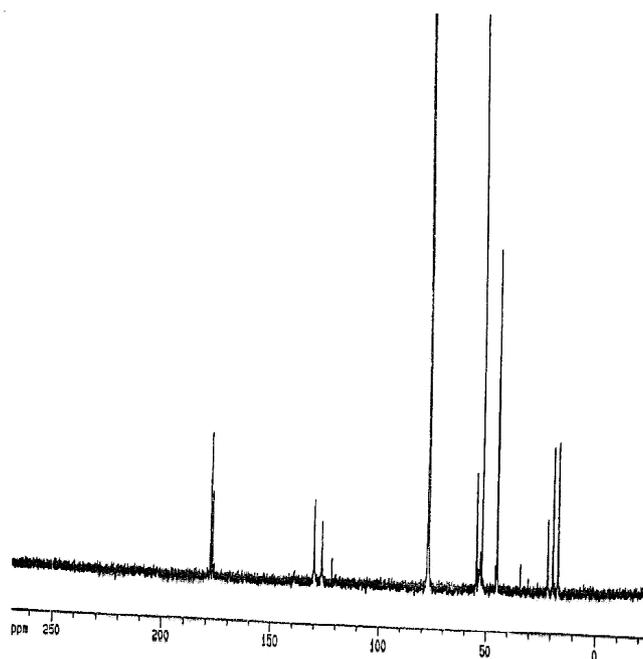

Fig. 4. ^{1}H NMR spectra of PMMA-b-PC copolymer prepared by using PMMA-Cl/CuBr/Bipyridine

all the block copolymers without much effect on polydispersity index. Fig. 5 show the GPC curve 3 of PMMA and PMMA-b-PPTC copolymer. Results of GPC analysis are summarized in Table-3.

The number average molecular weight in all block copolymers increased and was found to be in the range of 1000-1800. However high molecular weight PMMA *i.e.* M$_n$ of 4.8 × 10^4 with narrow PDI (1.17) could be prepared by using PMMA-X macroinitiator (M$_n = 1.25 \times 10^4$ and PDI = 1.31), isomerization of N-aryl citraconimides to N-aryl itaconimides or termination due to chain transfer reaction may be responsible for the low molecular weight of the second block.
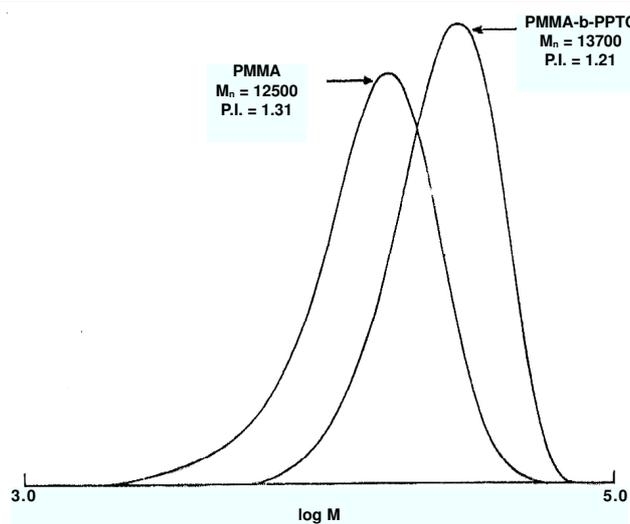
TABLE-2
MOLE FRACTION OF CITRACONIMIDE IN BLOCK COPOLYMERS PREPARED USING PMMA-Cl/CuBr/Bpy INITIATING SYSTEM

Polymer	Mole fraction of N-aryl citraconimide in copolymer calculate from	
	% Nitrogen content	^{1}H NMR
PMMA-b-PC	0.10	0.090
PMMA-b-PPC	0.09	0.080
PMMA-b-PMC	0.13	0.093
PMMA-b-POC	0.07	0.057
PMMA-b-PPTC	0.14	0.128

Fig. 5. GPC curve of PMMA and PMMA-b-PPTC copolymer

TABLE-3
GPC RESULT OF BLOCK COPOLYMERS OBTAINED FROM PMMA-Cl/CuBr/Bipy INITIATING SYSTEM

Polymer	M_n	Polydispersity index
PMMA*	1.25×10^4	1.31
PMMA-b-PC	1.40×10^4	1.29
PMMA-b-PPC	1.35×10^4	1.28
PMMA-b-PMC	1.34×10^4	1.32
PMMA-b-POC	1.33×10^4	1.43
PMMA-b-PPTC	1.37×10^4	1.21

*PMMA obtained from AIBN/FeCl₃.6H₂O/PPh₃ initiating system.

In order to investigate this fact, N-aryl citraconimide monomer (C, PC, MC and PTC) were heated separately in toluene at 90 ºC for different time intervals and % isomerization was calculated by recording ^{1}H NMR spectrum. ^{1}H NMR spectra were recorded at regular time intervals and ratio of signals at $\delta = 2.17 \pm 0.03$ ppm and $\delta = 5.76 \pm 0.03$ ppm was used for calculating % isomerization. The results obtained for % isomerization are given in Table-4. Intensity of resonance signal at δ 2.17 ± 0.03 ppm increased with increasing heating time and isomerization was found to be 32 %, 21 % and 23 % in case of MC, PC and C monomers, respectively after 6 days. On the other hand, *ca.* 40 % isomerization was observed in case of PTC monomer after 9 days. Fig. 6 show the ^{1}H NMR spectra of PTC obtained after 3,6 and 9 days.

Conclusion

The number average molecular weight (M_n) in block copolymers increased and was found to be in the range of 1000-1800.

TABLE-4
EFFECT OF HEATING TIME ON THE ISOMERISATION OF N-ARYL CITRACONIMIDES IN TOLUENE AT 90 ºC

Time (h)	Isomerisation (%) in N-aryl citraconimides			
	PTC	MC	PC	C
9	12.60	–	–	–
18	15.75	15.25	6.90	6.85
36	18.10	22.78	10.20	9.95
72	24.10	25.40	14.75	14.30
108	27.90	28.50	18.05	18.90
144	30.20	32.30	21.30	22.95
216	39.00	–	–	–
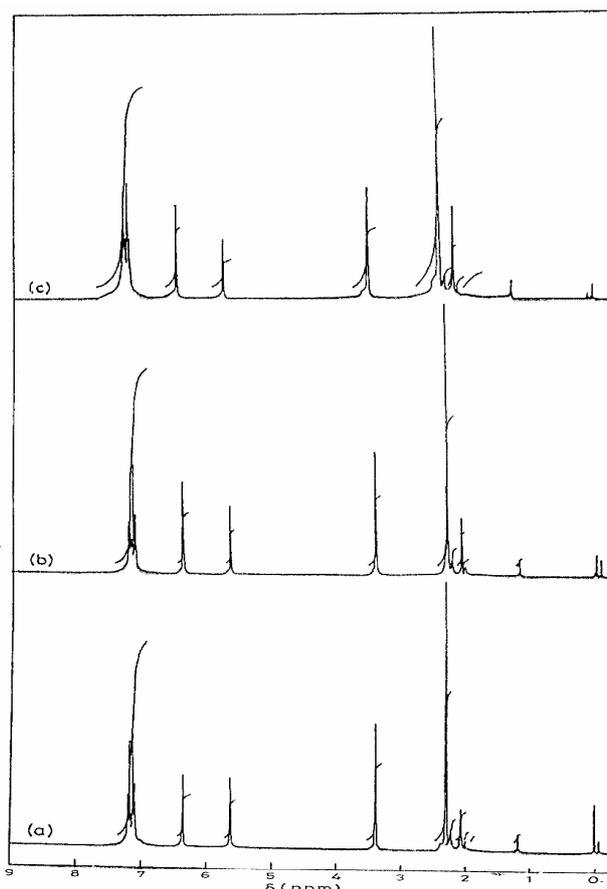
Fig. 6. ^{1}H NMR spectra of PTC monomer obtained after heating at 90 ºC in toluene for various intervals (a) 3 days (b) 6 days (c) 9 days

However high molecular weight PMMA *i.e.* Mn of 4.8×10^4 with narrow PDI (1.17) could be prepared by using PMMA-X macroinitiator ($M_n = 1.25 \times 10^4$ and PDI = 1.31). It is due to isomerization of N-aryl Citraconimides to N-aryl itaconimides or termination due to chain transfer reaction which is responsible for the low molecular weight of the second block.

REFERENCES

1. D.A. Shipp, J.L. Wang and K. Matyjaszewski, *Macromolecules*, **31**, 8005 (1998).
2. J. Xia, T. Johnson, S.C. Gaynor, K. Matyjaszewski and J. DeSimone, *Macromolecules*, **32**, 4802 (1999).
3. B. Reining, H. Keul and H. Hocker, *Polymer*, **40**, 3555 (1999).
4. H. Keul, A. Neumann, B. Reining and H. Hocker, *Macromol. Symp.*, **161**, 63 (2000).
5. M. Destarac, K. Matyjaszewski, E. Silverman, B. Ameduri and B. Boutevin, *Macromolecules*, **33**, 4613 (2000).
6. M.A.J. Schellekens, B. Klumperman and R. Vander Linde, *Macromol. Chem. Phys.*, **202**, 1595 (2001).
7. R. Karunakaran and J.P. Kennedy, *J. Polym. Sci. A*, **45**, 4284 (2007).
8. S.M. Kwak, J.H. Yeon and T.H. Yoon, *J. Polym. Sci. A*, **44**, 2567 (2006).
9. A.S. Brar and T. Saini, *J. Polym. Sci. A*, **43**, 2810 (2005).
10. S. Liu and A. Sen, *J. Polym. Sci. A*, **42**, 6175 (2004).