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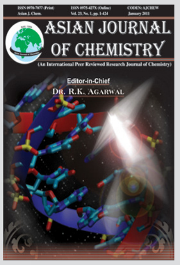

p-Nitrobenzyl Triphenyl Phosphonium Ylide as New Initiator in Polymerization of Ethylacrylate

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1,2-Dipolar compound containing phosphorus ylide (*p*-NBTPY) initiated radical polymerization of ethylacrylate in dioxane yielding syndiotactic polyethylacrylate, as evidenced by FTIR and ^{1}H NMR. It was investigated dilatometrically at 65 ± 0.1 ºC for 1 h under nitrogen atmosphere. The kinetic expression is $R_p \propto [I]^{0.4} [M]^{1.2}$. The system follows non-ideal kinetics because of primary radical termination. The activation energy and k_p^2/k_t were calculated as 53 kJ/mol and 0.15×10^{-2} mol L^{-1} s^{-1}, respectively. Thermal properties of polymer have been established with the help of DSC and TGA technique. The polymer has been characterized by MALDI-TOF. The absence of phosphorus in polymer matrix is confirmed from the scanning electron microscopy. The initiation is brought about by phenyl radical as evidenced from six hyperfine lines in electron spin resonance spectrum.

Key Words: Ethylacrylate, Non-ideal kinetics, Free radical polymerization.

INTRODUCTION

One of the area of interest has been the free radical polymerization of acrylates. Large efforts are made for better understanding of the kinetics, reaction mechanism of synthesis of polyacrylates. Among polyacrylates, polyethylacrylate is a high temperature resistant elastomer and has a superior resistance to degradation. It has immense applications in coating, textiles, finishing, paper saturant, leather finishing and oil resistant.

Rodica and Bazuin[1] plasticized polyethylacrylate ionomer by 4-decylaniline and accessed the cluster transition. Tong and Bazuin[2] also investigated, polyethylacrylate ionomer containing neutralized carboxylate groups. Hutton[3] and Nandi[4] polymerized ethylacrylate and studied the kinetics using AIBN as an initiator.

Ylide containing heteroatom like bismuth, antimony, arsenic, sulphur have also been reported as initiator[5,6], retarders[7] and degradative transfer agent[8] in polymerization of different vinyl monomers. However, the applications of phosphorus ylide is scarce[9]. Ylides are zwitter ionic compounds in which a carbonion is covalently bonded to a positively charged heteroatom.

Nandi *et al.*[4] observed that during polymerization of ethyl acrylate the system became highly viscous when AIBN was used as an initiator. It is due to the gelation problem during polymerization[10]. As a result a limited radical initiator have been reported. The literature reveals that ethylacrylate has not been initiated by any ylide.

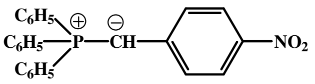
Phosphorus ylide have attracted much attention in synthetic and theoretical chemistry[11], reaction intermediates[12,13] and as polymerization catalyst[14]. Wittig reaction is always associated with a phosphorus ylide and this process which allows a C=C bond to be created at a specific point in a given molecule. It is the most striking utility of phosphorus ylide. Studies of the mechanisms of Wittig reaction and properties of ylides have evoked interest in and provided a substrate for the study of valence shell expansion by elements of the second and lower periods. Doering *et al.*[15] have provided a quantitative estimate of the importance of valence shell expansion of phosphorus in providing stabilization for an adjacent carbanion. The phosphorus carbon bond is resonance hybrid between a dipolar form I and a double bond form II.

$$\underset{\text{(I)}}{R_3\overset{+}{P}-\overset{-}{C}R_2} \longleftrightarrow \underset{\text{(II)}}{R_3P=CR_2}$$

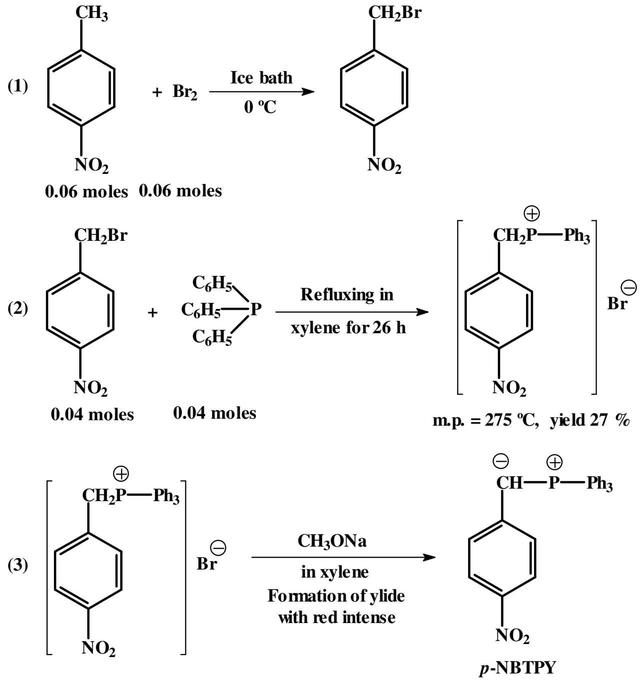
In previous system[16a,b,c] we have reported the applications of phosphorus ylides as an radical initiator. An attempt has been made in the present system, to establish phosphorus ylide as radical initiator in polymerization of ethyl acrylate.

EXPERIMENTAL

Ethyl acrylate (Merck) was purified by passing it through an alkali to remove inhibitor, washed with distilled water followed by vacuum distillation before polymerization. Triphenylphosphine (Merck) was used as received. Solvent were purified by usual methods[17]. *p*-Nitrobenzyl triphenyl phosphonium ylide (*p*-NBTPY) was prepared by the method detorled by McDonald and Campbell[18]. The ylide has following structure:



Briefly the synthesis of ylide is as follows:



Polymerization procedure: The polymerization of ethylacrylate was carried out in 1,4-dioxane at 65 ± 1 ºC for 1 h in dilatometer under nitrogen atmosphere. The polymer was precipitated with methanol and dried to constant weight to calculate the percentage conversion as well as rate of polymerization[19].

Measurements: Viscosity-average molecular weight ($\overline{M}_v$) of the polymer was determined in benzene at 30 ± 1 ºC with an Ubbelohde viscometer with the values of Mark-Houwink constant[20].

Using $$[\eta] = K(\overline{M}_v)^{\alpha}$$

where K = 27.7 × 10^{-3} mL/g

$\alpha = 0.67$

Characterization: The polymer was characterized by FTIR. The spectra was recorded on Perkin-Elmer 599B in dichloromethene. ^{1}H and ^{13}C NMR spectra was recorded with Varian 100 HA Jeol LA 400 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Diffraction scanning calorimetry was carried out using VAOB Dupont 2100 analyser, the weight of the sample was 5.679 mg. Thermogravimetric analysis was conducted in Perkin-Elmer, Pyris diamond, TGA analyzer, sample weight 6.073 mg at heating rate 15 ºC and temperature range 20-500 ºC. MALDI-TOF MS was run on a Micromass Tof Spec 2E instrument using a nitrogen 337 nm laser (4 ns Pulse). At least 40-50 shots are summed up. The matrix used is α-cyanohydroxy cinnamic acid dissolved in ACN:MeOH. The sample and matrix solutions were mixed together and 1 µL spotted on MALDI target. ESR spectra was performed in Bruker EMX ESR spectrometer model No. 1444. SEM analysis was performed in Jeol 840A scanning electron microscope.

RESULTS AND DISCUSSION

The ylide initiated radical polymerization of ethylacrylate. The reaction proceeded with an induction period of 2-9 min in all cases. It was observed that the system becomes highly viscous after 22 % conversion. However, we have restricted our studies upto 14 % conversion.

Effect of *p*-NBTPY concentration: The effect of *p*-NBTPY on the rate of polymerization was studied by varying [*p*-NBTPY] from 8.4 × 10^{-6}-42.0 × 10^{-6} mol L^{-1}, (Fig. 1) keeping the monomer concentration [EA] = 2.45 mol L^{-1} and temperature 65 ± ºC constant. The polymerization is associated with an induction period of 3-6 min. The rate of polymerization (Table-1) is a direct function of ylide concentration. The initiator exponent, calculated from the slope of the plot log R_p *versus* log [*p*-NBTPY], is 0.4 (Fig. 2). The value is lower than expected for ideal kinetics in radical polymerization. On increasing the initiator concentration the viscosity average molecular weight ($\overline{M}_v$) of the polymer decreases. The plot of $1/M_v$ *versus* [*p*-NBTPY] (Fig. 3) passes through the origin,

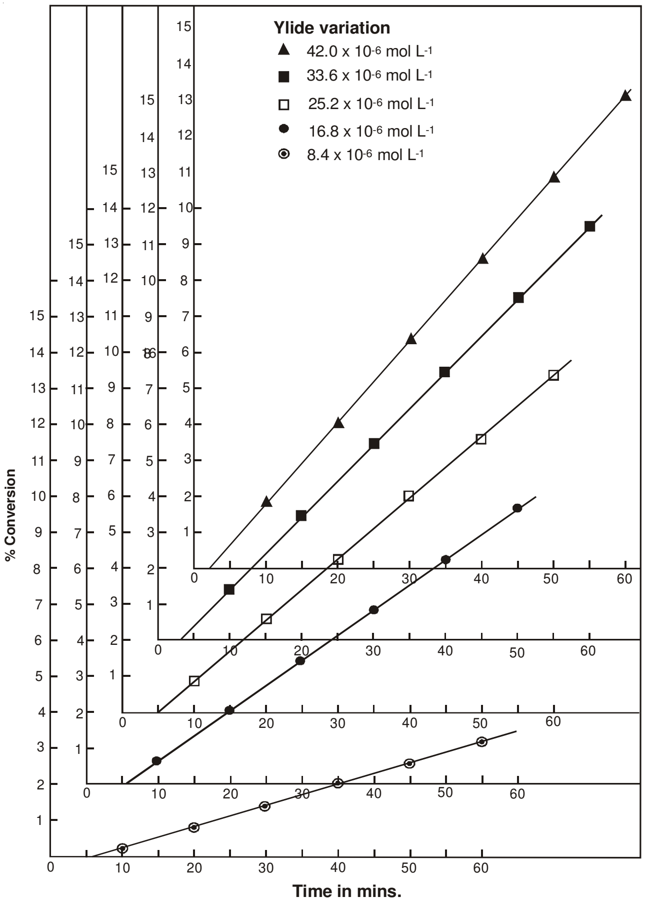


Fig. 1. Percentage of conversion *versus* time plot for the polymerization of ethylacrylate with [*p*-NBTPY] as radical initiator. [EA] = 2.45 mol L^{-1}, polymerization time = 60 min and polymerization temperature = 65 ± 0.1 ºC

TABLE-1
EFFECT OF *p*-NBTPY CONCENTRATION ON THE RATE OF POLYMERIZATION (R_p)

Run No.	*p*-NBTPY × 10^6 (mol L^{-1})	Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$\overline{M}_v$
1	8.4	3.2	2.60	147518
2	16.8	7.6	5.30	81304
3	25.2	9.3	5.70	65231
4	33.6	11.6	8.10	49236
5	42.0	13.3	9.39	43056

[EA] = 2.45 mol L^{-1}, Temp. = 65 ± 0.1 ºC; Time = 60 min

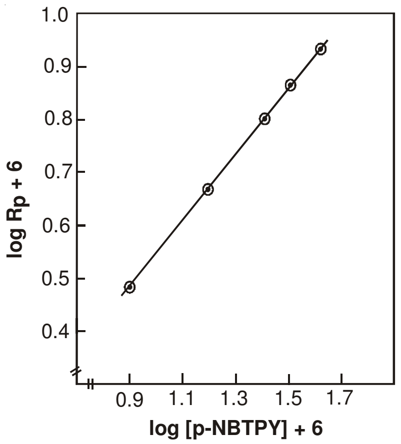


Fig. 2. Plot for log R_p *versus* log [*p*-NBTPY]; ethylacrylate = 2.45 mol L^{-1}, [*p*-NBTPY] = 25.2 × 10^{-6} mol L^{-1}, polymerization time = 60 min, temperature = 65 ± 0.1 ºC

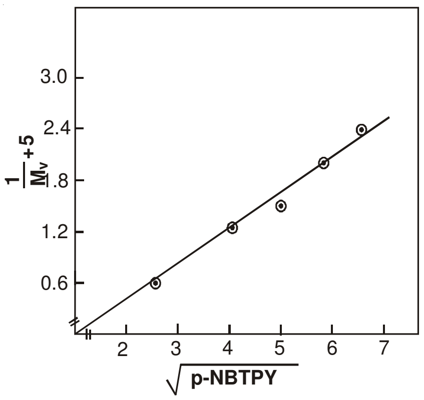


Fig. 3. Plot of $1/\overline{M}_n$ *versus* $\sqrt{[p-\text{NBTPY}]}$; [EA] = 2.45 mol L^{-1}, [*p*-NBTPY] = 25.2 × 10^{-6} mol L^{-1}, polymerization time = 60 min, polymerization temperature = 65 ± 0.1 ºC

which further confirms radical polymerization with bimolecular termination. The value for the ratio of the (propagation rate constant)^2 to the rate constant for termination k_p^2/k_t at 65 ºC has been calculated from the slope of $1/M_v$ *versus* [R_p/M^2] (Fig. 4) as 0.15 × 10^{-2} mol L^{-1} s^{-1}. Fukuda *et al.*[21] reported the value of k_p^2/k_t at 40 ºC as 4.32 × 10^{-4} mol L^{-1} s^{-1}. With the increase in temperature the value of k_p^2/k_t decreases.

Effect of monomer concentration: Effect of monomer on the rate of polymerization (R_p) was studied by varying the ethylacrylate concentration (Fig. 5) from 1.22 to 3.68 mol L^{-1}. Keeping the initiator concentration and temperature constant at 25.2 × 10^{-6} mol L^{-1} and 65 ± 0.1 ºC, respectively. A study of (Table-2) shows that the (R_p) is a direct function of ethylacrylate concentration. The monomer exponent value, calculated from

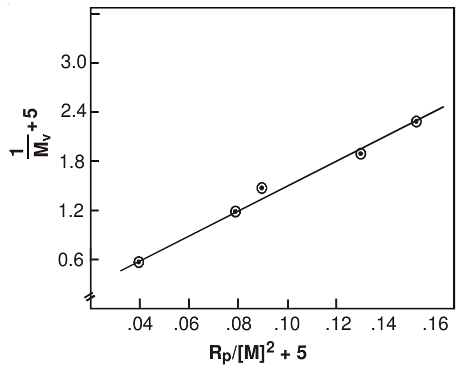


Fig. 4. Plot of $1/\overline{M}_n$ *versus* $R_p/[M]^2$, [EA] = 2.45 mol L^{-1}, [*p*-NBTPY] 25.2 × 10^{-6} mol L^{-1}, polymerization time = 60 min, polymerization temperature = 65 ± 0.1 ºC

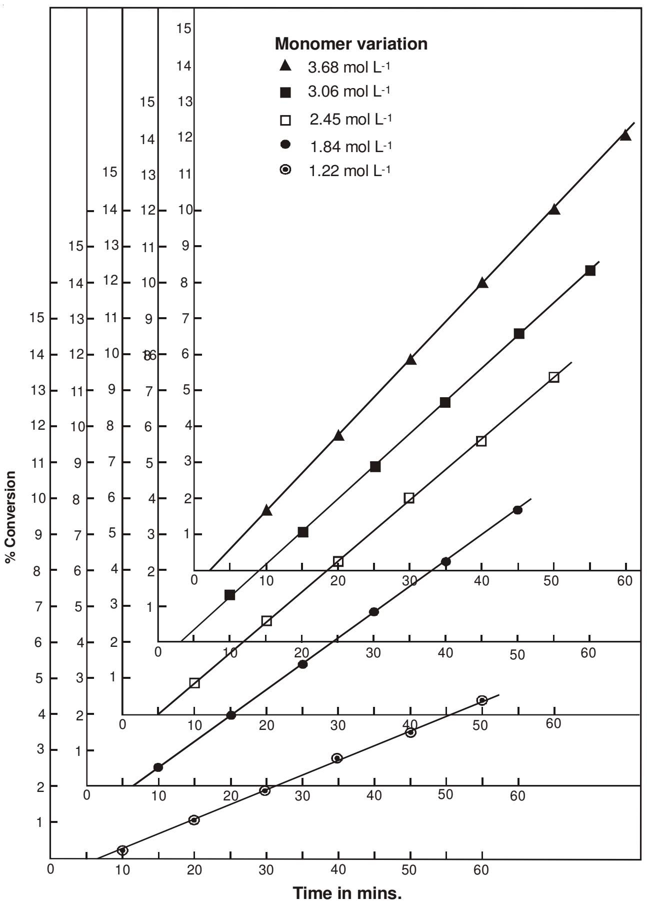


Fig. 5. Percentage of conversion *versus* time plot for the polymerization of ethylacrylate with [*p*-NBTPY] as radical initiator. [*p*-NBTPY] = 25.2 × 10^{-6} mol L^{-1}, polymerization time = 60 min and polymerization temperature = 65 ± 0.1 ºC

TABLE-2
EFFECT OF MONOMER CONCENTRATION ON THE RATE OF POLYMERIZATION (R_p) OF ETHYLACRYLAMIDE INITIATED BY *p*-NBTPY

Run No.	EA (mol L^{-1})	Conversion (%)	$R_p \times 10^6$ (mol L^{-1} s^{-1})	$\overline{M}_v$
1	1.22	4.3	1.72	39266
2	1.84	7.8	3.90	47551
3	2.45	9.3	5.70	65231
4	3.06	10.2	10.20	86231
5	3.68	12.0	14.10	115359

[*p*-NBTPY] = 25.2 × 10^6 mol L^{-1}, Temp. = 65 ± 0.1 ºC; Time = 60 min the slope of log R_p *versus* log [EA] (Fig. 6) is 1.2. This is higher than expected for an ideal kinetics in radical polymerization. The deviation in the values of initiator and monomer exponent suggests that the system follows non-ideal kinetics.

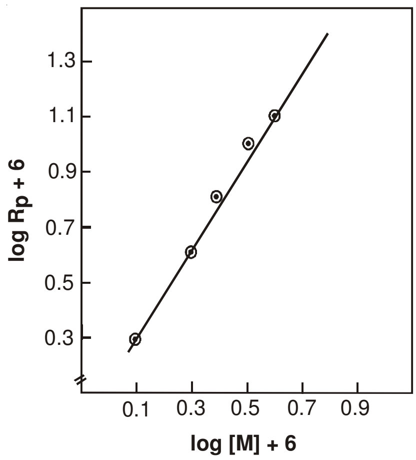


Fig. 6. Plot of log R_p *versus* log [EA]; [EA] = 2.45 mol L^{-1}, [*p*-NBTPY] 25.2×10^{-6} mol L^{-1}, polymerization time = 60 min, polymerization temperature = 65 ± 0.1 ºC

Cause of non-ideality: Various explanations[22a,b] for non-ideality in vinyl polymerization have been proposed but with limited success. It is now accepted that primary radical termination and degradative chain transfer are the most important cause of non-ideality. In order to detect primary radical termination, Deb and Meyerhoff[23] equation in the following form was used.

$$\log = \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.864 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2}$$

where f_k represents the fraction of free radical initiating chain growth, k_d = initiator decomposition rate constant, k_p = propagation rate constant, k_{prt} = primary radical termination constant and [M] = monomer concentration. Plot of log $R_p^2/[I][M]^2$ *versus* $R_p/[M]^2$ gave a negative slopes (Fig. 7) indicating significant primary radical termination. Such termination was further confirmed by the low initiator and high monomer exponent, which matches well with the literature value[24].

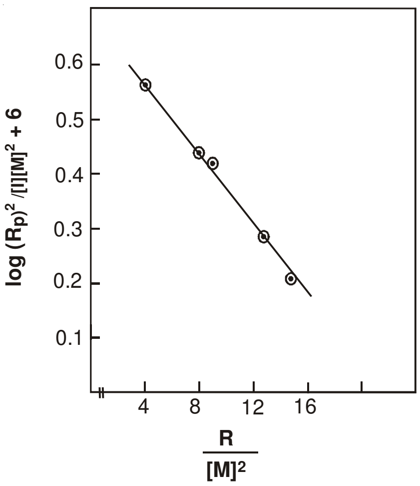


Fig. 7. Plot of log $R_p^2/[I][M]^2$ *versus* $R_p/[M]^2$

In order to detect degradative chain transfer Deb equation in the following form was used.

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2 k_{rtI}}{k_t k_{iI} k_p} C_I \frac{[I]}{[M]}$$

where C_I = initiator transfer constant, k_{rtI} = rate constant for degradative chain transfer to initiator, k_{iI} = initiator rate constant. The plot of log $R_p^2/[I][M]^2$ *versus* [I]/[M] did not give a negative slope. The degradative chain transfer does not seem most effective in present system because, it is apparent that such transfer is most effective at low polymerization rates[25] and the initiator exponent is greater than 0.5.

Effect of temperature: Polymerization was carried out at 55, 60, 65, 70 and 75 ºC (Fig. 8). The rate of polymerization (R_p) increases with increase in temperature. The overall activation energy, calculated from the linear Arrhenius plot is 53.0 kJ mol^{-1} (Fig. 9).

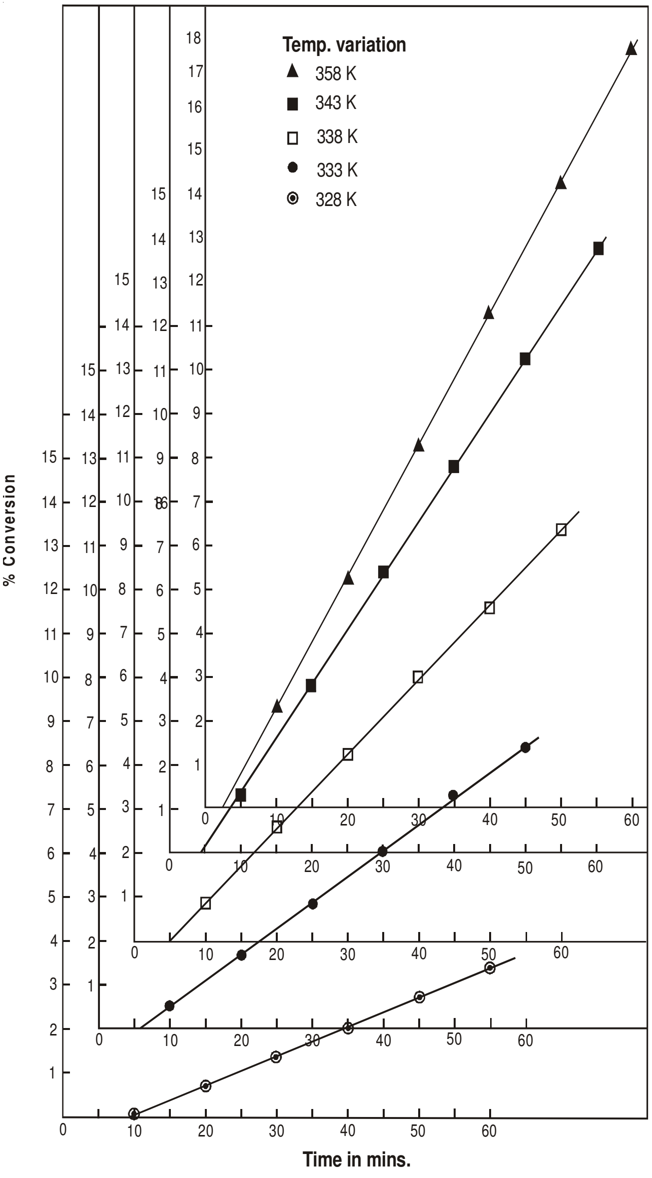


Fig. 8. Percentage of conversion *versus* time plot for the polymerization of ethylacrylate with [*p*-NBTPY] as radical initiator. [*p*-NBTPY] = $25.2.0 \times 10^{-6}$ mol L^{-1}, [EA] = 2.45 mol L^{-1}, polymerization time = 60 min

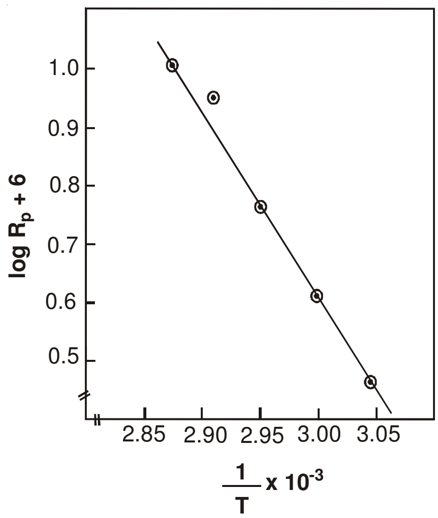


Fig. 9. Arrhenius plot of R_p *versus* polymerization temperature; [EA] = 2.45 mol L^{-1}, [*p*-NBTPY] 25.2 × 10^{-6} mol L^{-1}, polymerization time = 60 min

FTIR spectroscopy: FTIR spectrum (Fig. 10) of polyethylacrylate shows a sharp absorption band[26] at 1240 cm^{-1} confirming that the polyethylacrylate to be of syndiotactic nature. Absorption band at 1385 cm^{-1} was not observed, which refers to that of isotactic polyethylacrylate. A sharp band of carbonyl stretching vibration of the ester group appear at 1731 cm^{-1}. The band at 1026 and 2981 cm^{-1} appears due to C-O-C stretching of ester and aromatic phenyl, respectively.

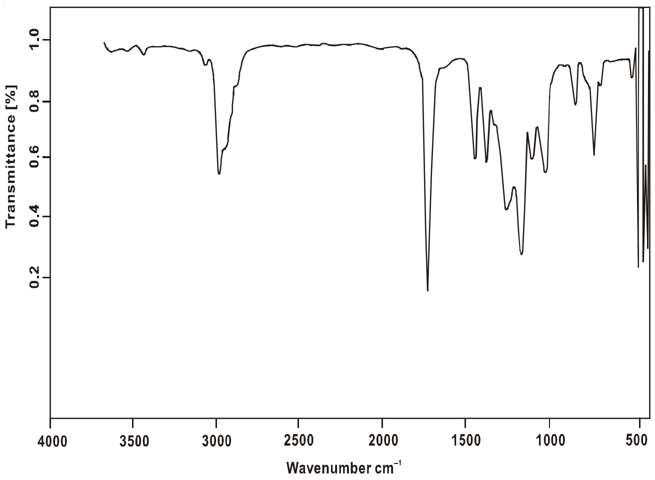


Fig. 10. FTIR spectral analysis of polyethylacrylate of run No. 3

^{1}H NMR spectroscopy: The ^{1}H NMR spectrum (Fig. 11) has been used to determine the stereoregularity of polyethylacrylate. It has been found that polyethylacrylate also gives a backbone proton spectrum similar to that of polymethylacrylate[27]. Ester methyl protons are located at δ 4.0 ppm. The tacticity of polymers are determined from the backbone methylene protons absorption as a triplet at δ 1.77, 1.82, 1.9 ppm confirming the syndiotactic nature of polymer. Yoshino *et al.*[28] observed the peaks ranging from δ 1.52 to 1.78 ppm due to isotactic methylene protons *trans* to carboxyl group and those from δ 1.97 to 2.25 ppm due to *gauche* conformation. There is no peak in this region. The peak of methine protons are observed at δ 2.6 ppm. Signals at δ 7.4-7.8 ppm corresponds to phenyl protons.

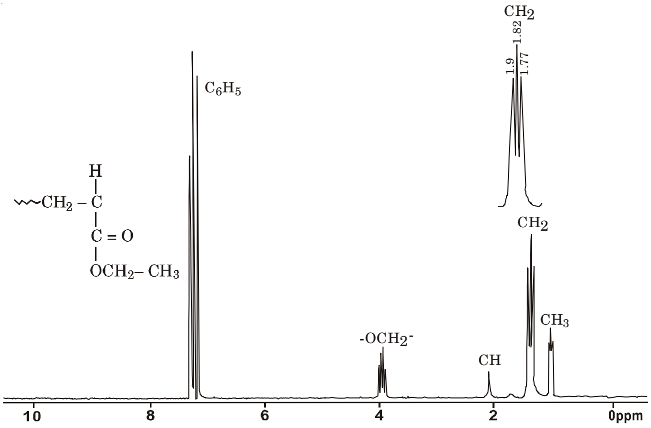


Fig. 11. ^{1}H NMR spectral analysis of polyethylacrylate run No. 3

^{13}C NMR spectroscopy: The ^{13}C NMR spectrum (Fig. 12) shows the carbon signals of -CH_3, -CH_2 at δ 12.5 ppm and δ 35 ppm, respectively. The backbone methine carbon signals appear at δ 41.3 ppm. The resonance signals around δ 58.5 and 172.5 ppm can be assigned, respectively to -OCH_2 and >C=O carbon in polyethylacrylate.

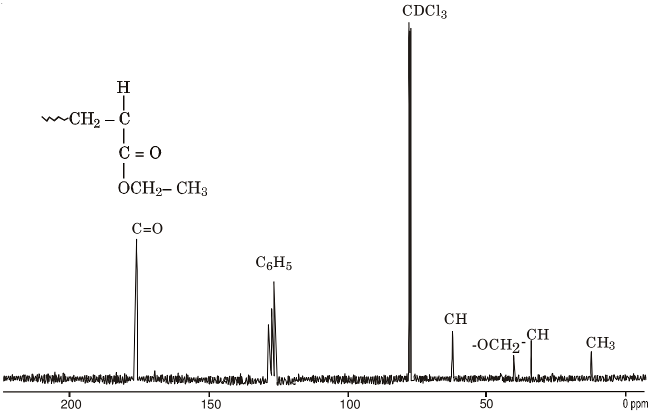


Fig. 12. ^{13}C NMR spectral analysis of polyethylacrylate run No. 3

DSC: DSC is a useful tool in the study of the glass transition temperature (T_g), kinetics of crystallization and melting of the polymers. Melting of polymer crystals is a complicated phenomena. It has been reported that the glass transition temperature[29] of polyethylacrylate is -24 °C for conventional and syndiotactic polyethyl acrylate and -25 °C for isotactic polyethylacylate. In present study, we could not study the T_g of the polymer due to lack of cooling facility in the instrument. The crystalline and melting temperature of polyethylacrylate is 117 and 402 ºC, respectively (Fig. 13). DSC data is used to calculate the percentage crystallinity[30] by using:

$$M_c = \frac{T^1}{T_m^*}$$

where M_c = total grams of polymer crystalline below T_c crystalline fraction (C_f) is calculated by dividing M_c by the total weight of sample.

$$C_f = \frac{M_c}{M_{total}}$$

$$\text{Crystallinity (\%)} = \text{Crystalline fraction} \times 100$$
$$= 0.049 \times 100 = 4.9\ \%$$

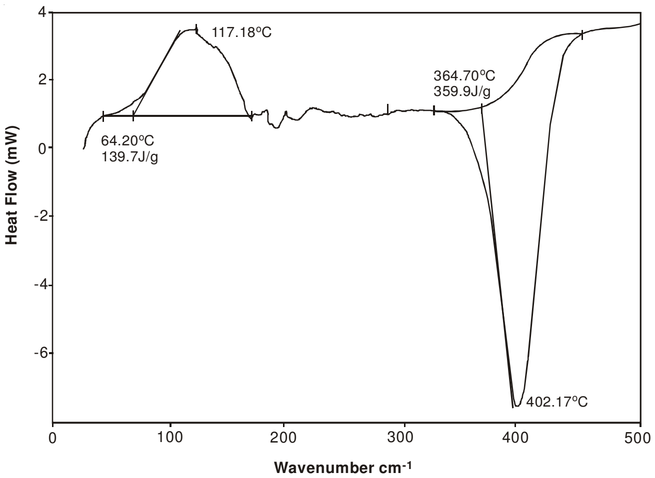


Fig. 13. DSC curve of polyethylacrylate run No. 3

TGA: TGA curve (Fig. 14) exhibits weight loss with temperature[31]. There are three distinct steps of weight loss.

20° - 270 °C = 6.07 %
271° - 350 °C = 19.8 %
351° - 450 °C = 80 %

The polymer is thermally stable upto 270 °C. TGA data shows a weight loss of 6.07 % upto 270 °C, which is attributed to the loss of absorbed water[32]. The weight loss between 271-350 °C and 351-450 °C are regions of minor and major weight loss and appear to be due to dehydration and extensive degradation of he polymer backbone chain[33]. Almost total volatilization of the polymer occurred above 450 °C.

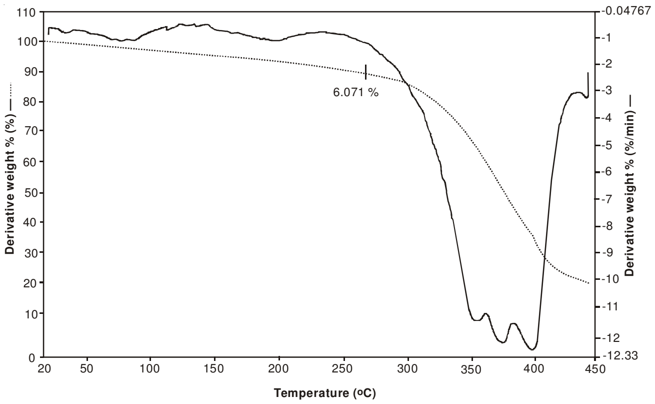


Fig. 14. TGA curves of polyethylacrylate run No. 3

SEM: The polymer matrix does not contain phosphorus. This has been confirmed by a qualitative test[34] using concentrate nitric acid and ammonium molybdate where yellow ppt. was not obtained. SEM report (Fig. 15) also show that the phosphorus is not incorporated in the polymer matrix.

MALDI-TOF: Matrix-assisted laser desorption ionization time of flight mass spectrometry is a soft ionization technique that has made it possible to ionize and analyze macromolecules with little to no fragmentation in a mass spectrometer[35,36]. Polymer molecules can be charged by proton transfer from an acidic matrix or by formation of an ion complex between the polymer and a suitable electron that has been added to the matrix. MALDI TOF is an indispensable tool for the determination of the structure, end groups and side reaction. The molecular ion peaks were clearly detected (Fig. 16) in a range from around m/z 400 to 6500. The ratio of mass to charge number for a macromolecule is given by the following equation[37]:

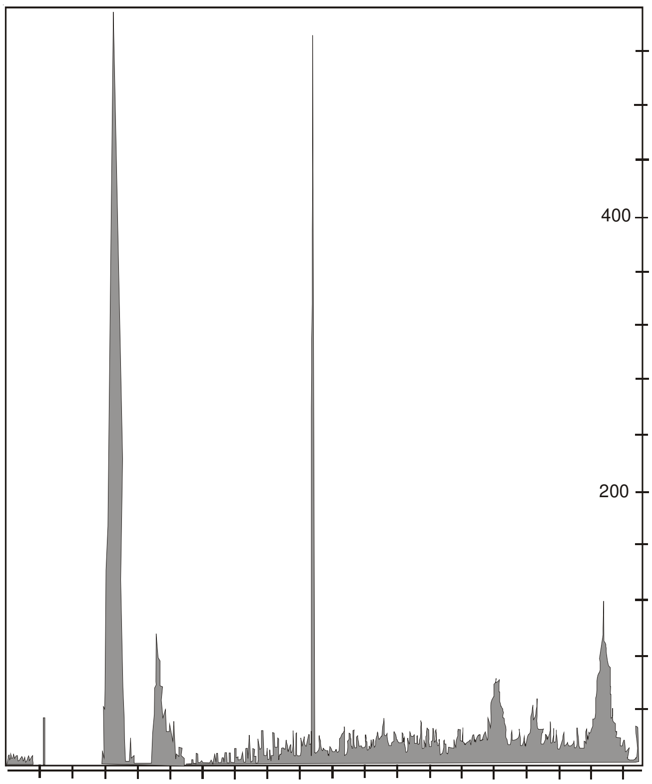


Fig. 15. SEM report of polyethylacrylate run No. 3

$$\left(\frac{m}{z}\right)^{z+} = n\cdot\frac{m_{mon}}{z} + \frac{m_{end}}{z} + m_{cat} - m_{elec}$$

where m_{mon} = molar mass of monomer repeat unit, n = number of monomer repeat unit, m_{end} = total molar mass of end groups, m_{cat} = molar mass of the cation, m_{elec} = mass of electron and z = charge of total mass of end group. The cationizing agent is K^+. Upon closer examination an addition peak family of low intensity, which hardly exceeds the base line noise, these peak can be attributed to molecules terminated by phenyl atom. The fraction of each polymer in the reaction mixture have been calculated from the above equation.

$$\frac{m}{z} = 77\times2 + n\times100 + 39$$

$$6393 = 154 + 100\,n + 39$$

$$n = 62$$

$$\left[C_6H_5\!\left(EA\right)_n\!C_6H_5\right]^+$$

Mechanism: It has been well reported[9] that the ylide undergoes homolysis to gives the phenyl radical, which participates in the initiation. ESR spectrum confirms (Fig. 17) the free radical mode of polymerization. The gyromagnetic ratio 'g' is calculated as 2.11, which is in agreement with the literature[38]. The spectrum shown six hyperfine lines and hyperfine constant as 3.74 (G)[39] confirming phenyl free radical responsible for polymerization.

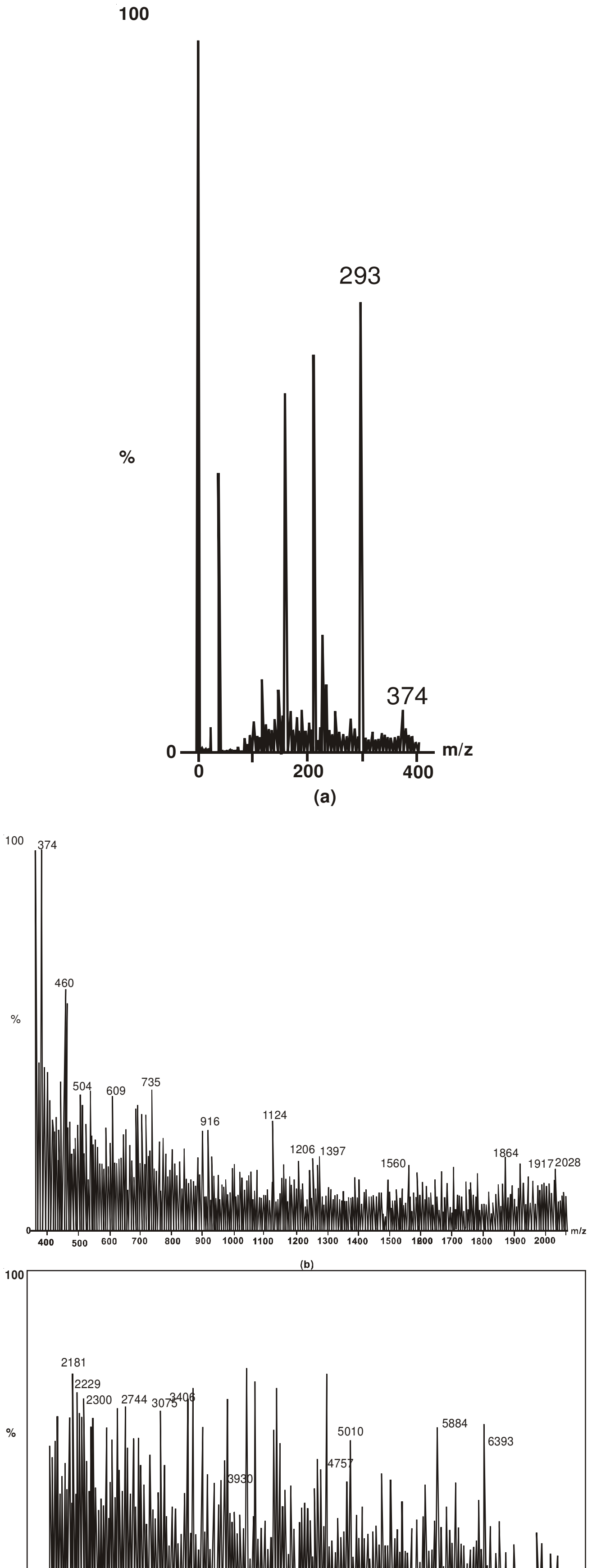


Fig. 16(a,b,c). MALDI TOFF spectra of polyethylacrylate run No. 3

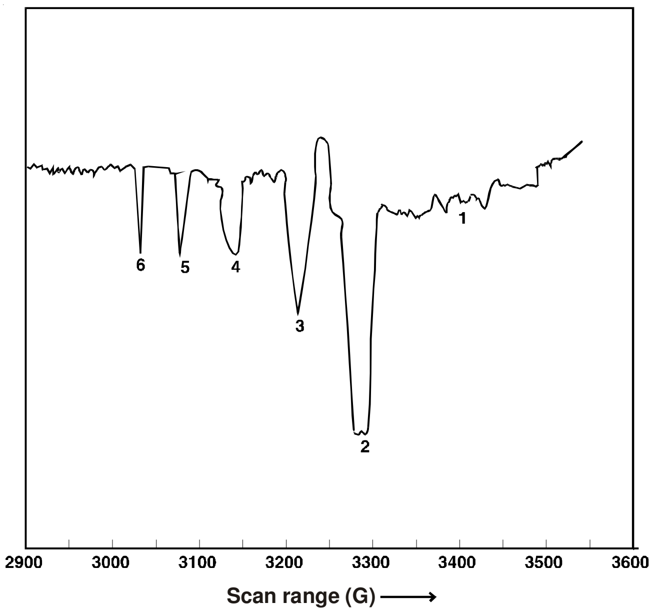
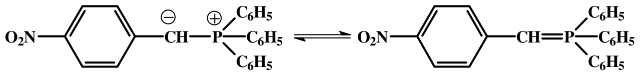
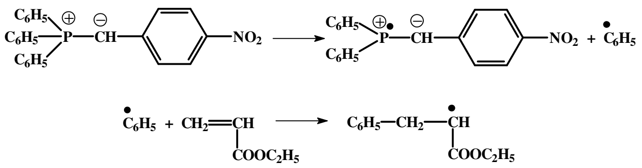


Fig. 17. ESR spectrum of polyethylacrylate run No. 3

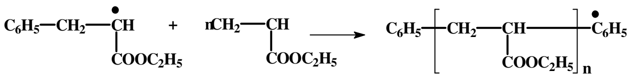
p-Nitrobenzyl triphenyl phosphonium ylide is considered to be the resource hybrid of following resonating structure:



Initiation:

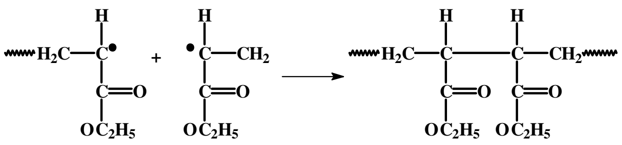


Propagation:



$$C_6H_5-CH_2-\overset{\bullet}{C}H(COOC_2H_5) + nCH_2-CH(COOC_2H_5) \longrightarrow C_6H_5-\left[CH_2-CH(COOC_2H_5)\right]_n-\overset{\bullet}{C}_6H_5$$

Termination:



Conclusion

p-Nitrobenzyl triphenyl phosphonium ylide is capable of initiating the polymerization of ethylacrylate in dioxane solution giving syndiotactic polymer as evidenced by FTIR, ^{1}H NMR spectral analysis. The polymer is stable upto 370 ºC. The phosphorus is not incorporated in the matrix and the initiation is bought by phenyl radical.

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REFERENCES

1. N.P. Rodica and C.G. Bazuin, *J. Polym. Sci. B. Polym. Phys.*, **29**, 1305 (1991).
2. X. Tong, C.G. Bazuin, *J. Polym. Sci. B, Polym. Phys.* **30**, 389 (1992).
3. J.C. Bevington, T.N. Huckerby and N.W.E. Hutton, *Eur. Polym. J.*, **20**, 525 (1984).
4. P.V.T. Raghuram and U.S. Nandi, *J. Polym. Sci. A-1*, **5**, 2005 (1967).
5. S. Tripathi, A.K. Srivastava, *J. Polym. Sci. A; Polym. Chem.*, **42**, 2060 (2004).
6. A.K. Srivastava and A.K. Chaurasia, *J. Chem. Sci.*, **116**, 55 (2004).
7. A.K. Shukla, S. Saini, P. Kumar, J.S.P. Rai and A.K. Srivastava, *J. Polym. Sci. A, Polym. Chem.*, **27**, 807 (1989).
8. R. Vasishtha, P. Kumar, S.K. Awasthi, U. Bhatnagar and A.K. Srivastava, *Colloid and Polym. Sci. (Steinkopff, Darmsdatt, Germany)*, **268**, 645 (1990).
9. S. Kondo, Y. Kondo and K. Tsuada, *J. Polym. Sci., Polym. Lett.*, **21**, 217 (1983).
10. N. Staudinger and E. Trommosdorff, *J. Am. Chem. Soc.*, **502**, 201 (1993).
11. H. Schmidbair, *Pure Appl. Chem.*, **52**, 1057 (1980).
12. A.W. Johnson, Ylide Chemistry, Academic Press, New York (1966).
13. D.G. Gilneany, *Chem. Rev.*, **94**, (1994).
14. M. Kobayashi, F. Samda and T. Endo, *Macromolecules*, **33**, 5384 (2000).
15. W.V. Doering and A.K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

16 (a) K. Prajapati and A. Varshney, *J. Polym. Sci. A, Polym. Chem.*, **43**, 6524 (2005); (b) K. Prajapati and A. Varshney, *J. Polym. Res.*, **13**, 97 (2006); (c) K. Prajapati and A. Varshney, *Polym. Int.*, **56**, 32 (2007).

17. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longmann, London, edn. 5, p. 397 (1989).
18. R.N. McDonald and T.W. Campbell, *J. Org. Chem.*, **24**, 1969 (1959).
19. S. Saini, R. Vasishtha, P. Shukla and A.K. Srivastava, *Macromolecules*, **22**, 1025 (1989).
20. J. Brandrup, E.H. Immergut, Polymer Hand Book: John Wiley & Sons, NewYork, London; Sydney: Toranto IV-10, edn. 2 (1975).
21. Yung-Dae Ma, P.S. Kim, K. Keiji and T. Fukuda, *Polymer*, **35**, 1375 (1994).

22a. M.S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).
22b. F. Tüdos, *Acta Chim. Hung.*, **43**, 397 (1965).

23. P.C. Deb and G. Meyerhoff, *Eur. Polym. J.*, **10**, 709 (1974).
24. U. Bhatnagar and A.K. Srivastava, *Macromol. Rep.*, **A-29**, (Supp. 1), 27 (1992).
25. P.C. Deb, *Eur. Polym. J.*, **11**, 31 (1975).
26. T. Uryu, H. Shiroki, M. Okada, K. Hosonuma and K. Matsuzaki, *J. Polym. Sci. A-1*, **9**, 2335 (1971).
27. K. Matsuzaki, T. Uryu and A. Ishida, *J. Polym. Sci. A-1*, **5**, 2167 (1967).
28. T. Yoshino, M. Shinomiya and J. Komiyama, *J. Am. Chem. Soc.*, **87**, 387 (1965).
29. J. Brandrup and E.H. Immergut, Polymer Hand Book: John Wiley & Sons, NewYork, London; Sydney: Toranto III-145, edn. 2 (1975).
30. S. Yadav and A.K. Srivastava, *Polym. Plastics, Tech. Engg.*, **43**, 1229 (2004).
31. P. Bajaj, M. Goyal and R.B. Chavan, *J. Appl. Polym. Sci.*, **51**, 423 (1994).
32. J.J. Maurer, D.J. Kustace and C.T. Ratcliffe, *Macromolecules*, **20**, 196 (1997).
33. D.H. Grant and N.J. Grassie, *Polymer*, **1**, 125 (1960).
34. F. Feigl and V. Anger, Spot Tests in Inorganic Analysis, Amsterdam: Oxford: NewYork, Elsevier, edn. 7, p. 96 (1975).
35. S.D. Hanton, *Chem. Rev.*, **101**, 527 (2001).
36. M.W.F. Nielen, *Mass Spectrom. Rev.*, **18**, 309 (1999).
37. L. Zuifang and S. Rimmer, *Macromolecules*, **35**, 1200 (2002).
38. W.A. Pryar, Free Radicals, McGraw-Hill, New York, p. 22 (1966).
39. A.K. Srivastava and M. Kaur, *Macromol. Rapid Commun.*, **21**, 291 (2000).