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Polyurethane-polymethacrylic acid multi-block copolymers and their anionomers through "living" radical mechanism

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Summary

Polyurethane-polymethacrylic acid multi-block copolymers were synthesized from tetraphenylethane based polyurethane iniferter. Number of polymethacrylic acid blocks and molecular weight of block copolymers increased with increasing polymerization time which proves that the formation of block copolymers is through a "living" radical mechanism. The multi-block copolymers obtained were converted into their sodium anionomers. The multi-block copolymers and their anionomers have been characterized by FTIR, FTNMR and DSC analysis.

Introduction

Iniferter is an *ini*tiator, trans*fer* agent and/or *ter*minator in radical polymerization (1). Primary radical termination predominantly occur in iniferter polymerization (2). If the polymers/oligomers obtained through iniferters initiate further polymerization of vinyl monomers, then the system is termed as living radical polymerization (3). When the chain breaking reactions are minimum and the reversible termination is maximum then the system is called "living" radical polymerization (4). Here the quotation marks denote the meager presence of chain breaking reactions along with reversible termination. Recently "living" radical polymerization of vinyl monomers through 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) has been studied in detail (5-7). Block copolymers have a unique microphase morphology when compared to other copolymers. Since single step polymerization processes do not always give block copolymers, a number of synthetic strategies have been used (8). Polyurethane (PU)-polyvinyl block copolymers can be easily prepared from isocyanate terminated prepolymers and telechelic hydroxy terminated vinyl polymers. Conventionally azo initiators (9) are used to prepare telechelic polymers. But telechelic polymers with exact bi functionality could not be prepared via radical mechanism (10). Hence PU macroazoinitiators have been used to synthesize PU-polyvinyl block copolymers (11,12). The control over molecular weight of vinyl blocks in these block copolymers is still a problem. To over come this, tetraphenylethane based PU macroiniferters, prepared from isocyanate terminated prepolymer and 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED), has been used to polymerize methacrylic acid (MAA) and results are presented in this paper. Since tetraphenylethane iniferters follow "living" radical mechanism, the controlled incorporation of MAA units into the PU blocks is possible by

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just changing polymerization time. This method offers a novel route to synthesize hydrophobic-hydrophilic multi block copolymers.

Experimental

Materials

Toluene diisocyanate (TDI) (80% 2,4 and 20% 2,6 isomeric mixture) and dibutyltin dilaurate (DBTDL) were used as received from Aldrich, USA. Poly(tetramethyleneoxide) glycol (Aldrich, USA) of molecular weight 1000 (PTMG-1000) was used after drying by heating at 105°C under vacuum. MAA (Aldrich, USA) was distilled at reduced pressure and middle portion was stored at 0-4° C until use. Analytical grade N,N-dimethylformamide (DMF) and methyl ethyl ketone (MEK) were distilled and the middle portions were used after storing over type 4A molecular sieves. TPED was prepared (13) from benzophenone and 2-propanol. All other chemicals used were analytical grades and were used as received.

Characterization techniques

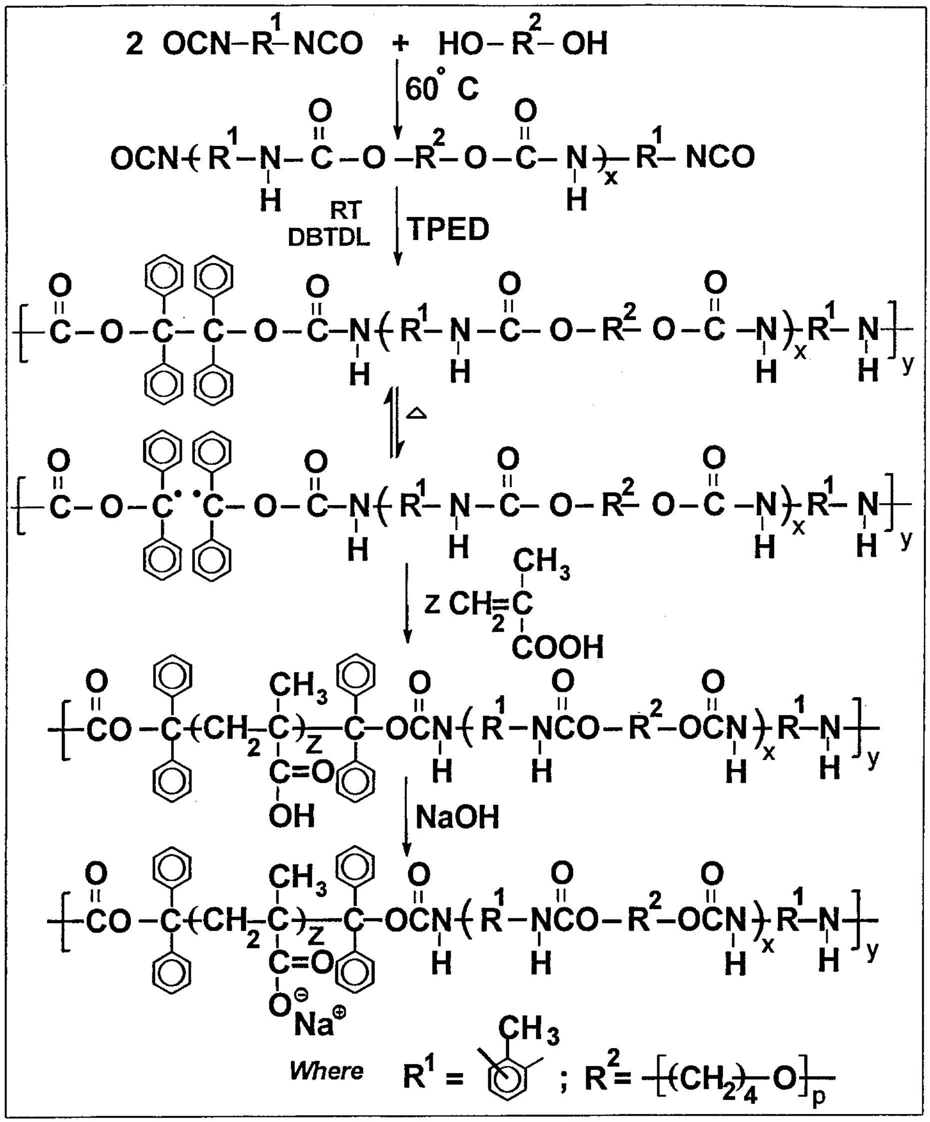
Number average ($\overline{M}_n$), weight average ($\overline{M}_w$) molecular weights and MWDs ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) using Waters Liquid chromatograph equipped with a 410 RI Detector and four μ styragel columns. DMF (0.01% LiBr added) was used as an eluent at a flow rate of 1.0 mL/min. and the molecular weight calibrations were done using polystyrene standards. The fourier transform infra-red (FT-IR) spectra were recorded as a KBr pellet on a Nicolet Impact 400 FT-IR spectrophotometer. Fourier transform nuclear magnetic resonance (FT-NMR) spectra were recorded on a Bruker MSLp 300 MHz NMR instrument using deuterated dimethyl sulfoxide as the solvent. Differential scanning calorimetry (DSC) was carried out using a Du Pont 910 DSC instrument at a heating rate of 10° C/min N_2 atmosphere.

Synthesis of polyurethane-polymethacrylic acid (PU-PMAA) multi-block copolymers and their sodium anionomers

Isocyanate terminated prepolymer was prepared by reacting two moles of TDI and one mole of PTMG-1000 at 60°C. This was chain extended by TPED at room temperature using DBTDL as a catalyst to obtain PU macroiniferter (14). Block copolymerization was carried out in sealed cylindrical pyrex tubes at 70°C. The detailed polymerization procedure of methyl methacrylate polymerization (15) was adopted here also. Acetone and distilled water were used to extract the PUs and homo-PMAA respectively form block copolymers. Conversion was calculated in three different ways as given in Table 1. PU-PMAA multi-block copolymeric ionomers were prepared by neutralizing DMF solution of PU-PMAA multi-block copolymers with aqueous NaOH using phenolphthalein as a indicator.

Results and Discussion

In our previous papers, novel PU iniferters were synthesized from equal moles of diisocyanates (16,17) and TPED. These iniferters were used to polymerize vinyl monomers (15-18) through "living" radical mechanism. Since the PU iniferter was synthesized from equal moles of diisocyanates and TPED, the tetraphenylethane groups were separated by organic moieties and hence the resulting vinyl polymers were only homopolymers. In this paper, PU macroiniferter consist of tetraphenylethane groups in between PU blocks are synthesized from isocyanate terminated prepolymers and TPED.


2 OCN–R¹–NCO + HO–R²–OH
60° C
RT
DBTDL
TPED
△
z CH₂=C(CH₃)COOH
NaOH
Where R¹ = ; R² = –[(CH₂)₄–O]ₚ–

SCHEME 1

This macroiniferter yields PU-PMAA multi block copolymers in the presence of MAA as given in scheme 1. Table 1 gives the results of block copolymerization of MAA using PU macroiniferter. These results show that PU macroiniferter initiates MAA polymerization. In this system both conversion (calculated in three different ways as given in Table 1) and $\overline{M}_n$ increase with increasing polymerization time. This is a typical result for "living" radical polymerization (3,14-18).

Fig. 1 shows FT-IR spectra PU macroiniferter, PU-PMAA multi-block copolymer (obtained at 48 hour; cf. Table 1) and its sodium anionomer. The peak at about 1700 cm^{-1} is due to the carbonyl stretching of urethane groups. This peak is very intense in the case of the block copolymer due to the presence of carbonyl group of PMAA block, when compared to PU iniferter. On conversion of COOH to COONa this peak intensity decreases and the peak at 1600 cm^{-1} (due to aromatic C=C stretching and COO^- of anionomer) increases. This is ample proof for the conversion of PU-PMAA multi-block copolymer into its anionomer. The peak at about 3300 cm^{-1} corresponds to N-H stretching vibrations. Fig. 2 shows the ^1H FT-NMR spectrum of PU-PMAA block copolymer (obtained at 48 hour; cf. Table 1). The peaks at about 8.1, 8.8 and 9.5 ppm are due to the N-H protons of urethane linkages. The $-CH_3$ protons from TDI units are observed as a doublet at 2.0 and 2.1 ppm. The peaks corresponding to aromaticprotons from TPED and

Table 1. Block copolymerization of MAA with PU macroiniferter at 70° C in DMF[a].

Sl. No.	Time (hr)	Conversion(%)			GPC results[b]		
		Q	R	S	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
1	0	13.07	-	-	5.17	10.02	1.94
2	1	14.32	5.09	35.54	5.57	10.91	1.96
3	3	15.83	5.96	37.64	6.04	12.39	2.05
4	6	18.47	7.38	39.95	6.73	15.06	2.24
5	9	22.37	9.76	43.65	7.47	16.21	2.17
6	12	25.84	12.55	48.56	8.09	16.67	2.06
7	18	31.64	16.85	53.24	8.64	17.63	2.04
8	24	37.61	22.05	58.64	9.01	18.12	2.01
9	36	42.76	26.23	61.35	9.44	18.59	1.97
10	48	48.00	31.38	65.37	9.95	19.10	1.92

[a] $[MAA]_0$ = 2.0 mol/L.; $[\text{PU macroiniferter}]_0$ = 2.66 g/dL.

[b] After extraction of homopolymers, using acetone and distilled water; the value at 0 time is for PU macroiniferter.

$$Q = \frac{\text{Weight of solid products before extraction of homopolymers x 100}}{\text{Initial weight of PU macroiniferter and MAA taken}}$$

$$R = \frac{\text{Weight of PU-PMAA after extraction of homopolymers x 100}}{\text{Initial weight of PU macroiniferter and MAA taken}}$$

$$S = \frac{\text{Weight of PU-PMAA after extraction of homopolymers x 100}}{\text{Weight of solid products before extraction of homopolymers}}$$

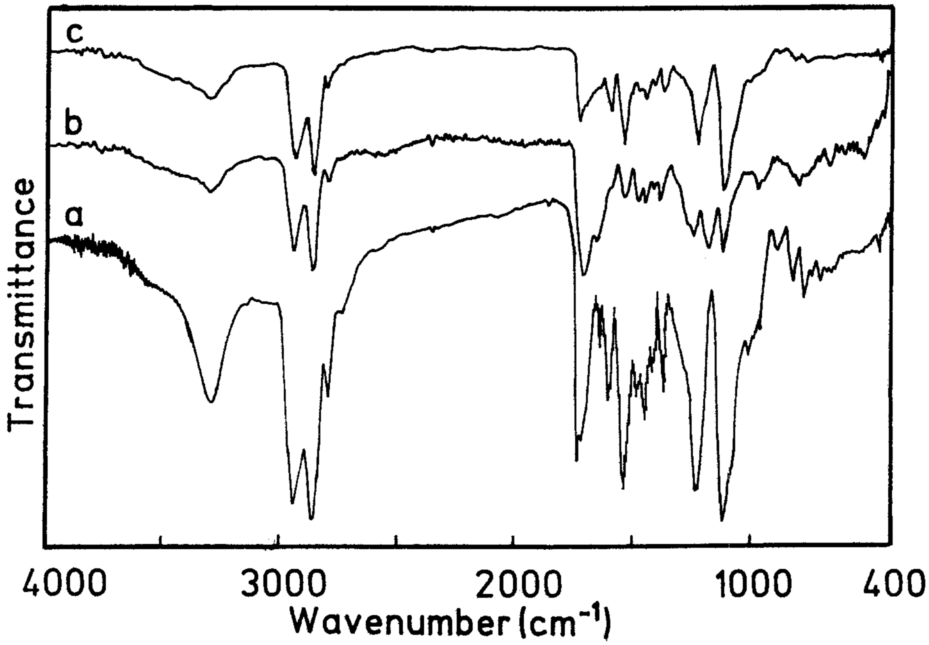


Fig.1. FTIR spectra of a) PU macroiniferter b) PU-PMAA multi-block copolymer and c) PU-PMAA multi-block copolymeric sodium anionomer.

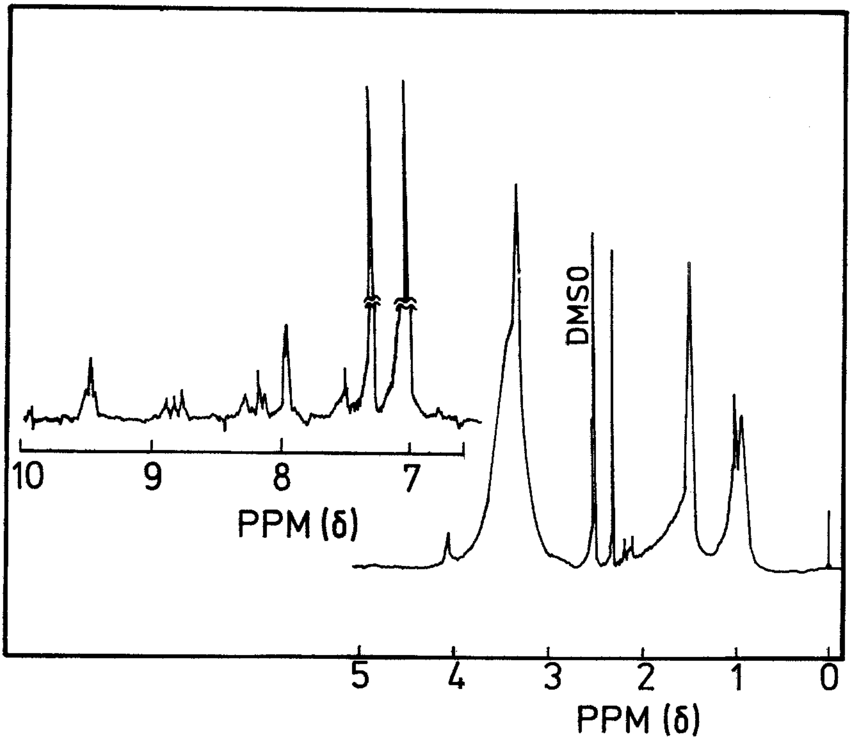


Fig.2. ^{1}H FTNMR spectrum of PU-PMAA multi-block copolymer.

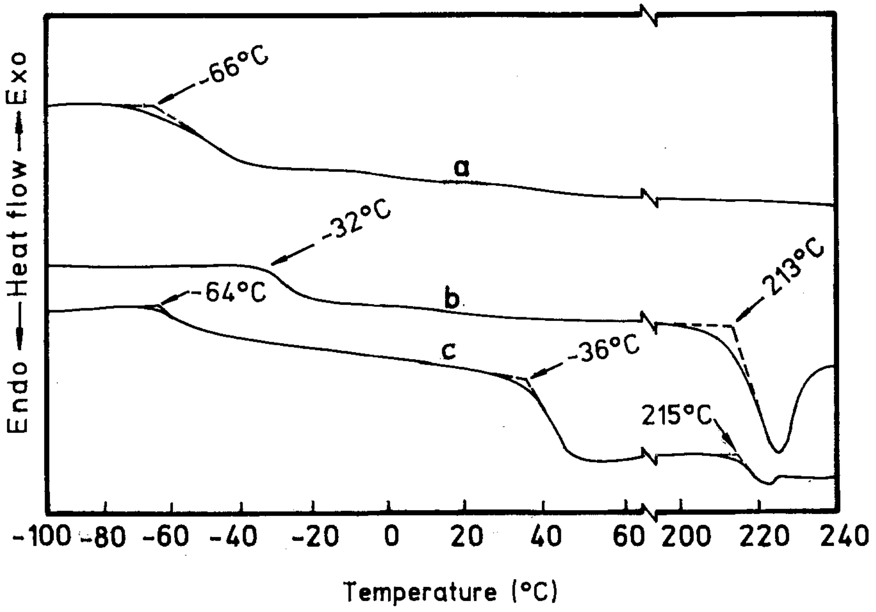


Fig.3. DSC curves of a) PU macroiniferter b) PU-PMAA multi-block copolymer and c) PU-PMAA multi-block copolymeric sodium anionomer.

TDI units are observed between 7 to 7.5 ppm.The aliphatic protons of PTMG unit present in the -CH_2, -O-CH_2 and -O-CH_2 adjacent to urethane groups are observed at about 1.5, 3.3 and 4.1 ppm respectively. The methylene protons adjacent to ether linkages (-O-CH_2-) which resonate around 3.3 ppm merge with the water signal present in DMSO-d_6 solvent leading to broadening of the peak here. The presence of peak around 1.0 ppm is due to the backbone CH_2 protons of PMAA units. The CH_3 protons present in PMAA blocks are observed 2.3 ppm. This result confirms that the PMAA block is incorporated in between PU block as given in Scheme 1.

Fig. 3 gives DSC curves of PU macroiniferter, PU-PMAA multi-block copolymer (obtained at 48 hour; cf. Tab. 1) and its sodium anionomer. The block copolymer shows two T_gs for PU and PMAA blocks. This is another evidence for the formation of PU-PMAA multi-block copolymer. Here, PU-PMAA multi-block copolymer shows higher T_g than that of its parent PU macroiniferter. On conversion of block copolymer into anionomer three endotherms corresponding to the T_gs of soft segment (polyol) of PU, hard segment (comprising of TDI and chain extender) and PMAA blocks, respectively. When the block copolymer is converted into its anionomer, realignment of hydrogen bonding takes place thereby resulting in a microphase separation. Due to this microphase separation separate T_g is observed for the hard segment also, which is not generally pronounced. Since in the anionomer, the hard segment is less dispersed in the soft segment, T_g of the soft segment shifts to lower temperature.

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References

1. Otsu T, Yoshida M (1982) Makromol Chem, Rapid Commun 3: 27
2. Bledzki A, Braun D, Titzschkau K (1987) Makromol Chem 188: 2061
3. Otsu T, Yoshida M, Tazaki T (1982) Makromol Chem, Rapid Commun 3: 133
4. Greszta D, Mardare D, Matyjaszewski K (1994) Macromolecules 27: 638
5. Veregin RPN, Georges MK, Hamer GK, Kazmaier PM (1995) Macromolecules 28: 4391
6. Matyjaszewski K (1994) J Macromol Sci, Pure Appl Chem A31: 989
7. Mardare D, Matyjaszewski K (1994) Macromolecules 27: 645
8. Riess C, Hurtrez G, Bahadur P (1985) in Encyc Polym Sci Eng 2: 324
9. Reed SF, (1972) J Polym Sci Part A-1 10: 2493
10. Heitz W (1986) Angew Makromol Chem 145/146: 37
11. Kinoshita H, Syoji A, Ooka M, Tanaka N, Araki T (1993) Makromol Chem 194: 829
12. Kinoshita H, Ooka M, Tanaka N, Araki T (1993) Makromol Chem 194: 2335
13. "Vogel's Textbook of Practical Organic Chemistry" 4th ed, ELBS/Longman publ, England 1987, p 359
14. Tharanikkarasu K (1995) Ph.D Thesis, University of Madras
15. Tharanikkarasu K, Ganga Radhakrishnan (1996) J Macromol Chem-Pure Appl Chem A33: 417
16. Tharanikkarasu K, Ganga Radhakrishnan (1994) Eur Polym J 30: 1351
17. Tharanikkarasu K, Vijitha Thankam C, Ganga Radhakrishnan, Polymer (Communicated)
18. Tharanikkarasu K, Ganga Radhakrishnan (1996) J Polym Sci, Polym Chem Edn 34: 1723