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G. N. Mahesh[a]; K. Tharanikkarasu[a]; S. Ramesh[a]; Ganga Radhakrishnan[a]
[a] Polymer Division, Central Leather Research Institute Adayar, Madras, India

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NOVEL POLYURETHANE MULTIBLOCK COPOLYMERS AND THEIR ZWITTERIONOMERS USING A POLYURETHANE MACROINIFERTER

G. N. MAHESH, K. THARANIKKARASU, S. RAMESH, and
GANGA RADHAKRISHNAN*

Polymer Division
Central Leather Research Institute
Adayar, Madras-600 020, Tamil Nadu, India

ABSTRACT

Polyurethane–poly(4-vinylpyridine) multiblock copolymers have been prepared by the decomposition of a tetraphenylethane-based polyurethane macroiniferter in the presence of 4-vinylpyridine. The increase in the molecular weight and conversion with an increase in polymerization time proves the "living" radical mechanism. The polyurethane-poly(4-vinylpyridine) multiblock copolymers so obtained were converted into their zwitterionomers by treating with γ-propane sultone. Both block copolymers and their zwitterionomers have been characterized using spectral and thermal techniques.

INTRODUCTION

Polymers with a hydrophobic backbone containing a relatively small number of ionic groups are referred to as ionomers. The most well-studied ionomeric polymer materials are polyethylene-*co*-methacrylic acid, sulfonated polystyrene, various copolymers of vinylpyridine, and copolymers of acrylic and methacrylic acids with different monomers. The above-mentioned ionomers have gained considerable importance as engineering, industrial, and domestic commodities [1, 2]. Pyridine-containing polymers have generated a lot of interest due to their ability to quarternize the tertiary nitrogen to prepare ionic polymers [3–6]. In the field of ionomer blends, pyridine-containing polymers have been used to study the mixing behavior of polymers [7-9]. Polyurethanes containing ionic groups are a very important class of materials which can be designed according to the end user needs. The properties of these materials can be made to vary from water repellant to completely water soluble. The principle ways of introducing ionic moieties into the polyurethane backbone have been 1) introduction of potential ionic sites at the chain extension stage [10-27] and 2) postpolymer modification [28-31].

Similar to living anionic polymerization [32], living radical polymerization was proposed by Otsu et al. [33] in order to improve chemoselectivity of radical polymerization. Usually if the bimolecular irreversible termination occurs to a small extent along with reversible termination, then the system is termed as "living" radical polymerization [34]. Irreversible terminations are minimized in "living" radical polymerization by reversible deactivation of growing free radicals. This kind of deactivation of the growing free radical can be brought about by reversible cleavage of covalent species (iniferters: *ini*tiators, trans*fer* agents, and/or *ter*minators) [33], formation of persistent radicals [35, 36], and using degenerative transfer agents [37]. Tetraphenylethane and disulfide derivatives are major iniferters which follow "living" radical polymerization [33, 38].

The importance that block copolymers have gained is due to their microphase morphology. Polyurethane–vinyl block copolymers are specialty high performance materials which can be used as thermoplastic elastomers. Telechelic hydroxyl-terminated vinyl polymers can be used as precursors for the preparation of polyurethane–vinyl block copolymers, but telechelic vinyl polymers with difunctionality cannot be easily prepared [39, 40]. Hence, polyurethane macroazoinitiators have been prepared and used to synthesize polyurethane–vinyl block copolymers [41, 42]. Even in these cases the vinyl block lengths cannot be controlled. Silicone-based tetraphenylethane macroiniferters [43, 44] and disulfide-based polyurethane iniferters [45, 46] have been used to prepare well-defined polymers through a "living" radical mechanism. In continuation of our research on tetraphenylethane iniferters [47-49], in this paper the synthesis and characterization of polyurethane–poly(4-vinylpyridine) (PU–PVP) multiblock copolymers prepared by the decomposition of a polyurethane macroiniferter containing tetraphenylethane groups between polyurethane blocks in the presence of 4-vinylpyridine (4VP) and their subsequent conversion to zwitterionomers are discussed. This method offers very efficient control over the levels of 4VP incorporation in the polyurethane by just changing the duration of polymerization.

EXPERIMENTAL

Materials

Analytical grade *N*,*N*-dimethylformamide (DMF) and methyl ethyl ketone (MEK) were distilled, and the middle portions were used after storing over type 4Å molecular sieves. Dibutyltin dilaurate (DBTDL) and a mixture of 80% 2,4- and 20% 2,6-toluene diisocyanate (TDI) were used as received from Aldrich, USA. Poly(tetramethyleneoxide) glycol of molecular weight 1000 (PTMG-1000, Aldrich, USA) was used as received after drying it by heating at 105°C under high vacuum for 2 hours. The inhibitor present in 4VP (Aldrich, USA) was removed by washing with 5% aqueous NaOH, washed again with distilled water, and stored over anhydrous sodium sulfate. It was then distilled at reduced pressure, and the middle portion was stored at 0–4°C until use. γ-Propane sultone (Aldrich, USA) was used as received. All other chemicals used were analytical grades and were used as received. 1,1,2,2-Tetraphenyl-1,2-ethanediol (TPED) was prepared from benzophenone and 2-propanol [50].

Characterization Techniques

Number-average ($\overline{M}_n$) and weight-average ($\overline{M}_w$) molecular weights and MWDs ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) using a Waters Liquid Chromatograph equipped with a 410 differential refractometer (RI Detector) and four μ-Styragel columns (10^6, 10^5, 10^4, and 10^3 Å) in series. 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 concentration and volume of polymer solutions injected were kept constant to enable comparison of the GPC curves at different polymerization times. The Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets 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 dimethylsulfoxide as the solvent and tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) analysis was carried out using a DuPont 910 DSC instrument at a heating rate of 10°C/min, and thermogravimetric analysis (TGA) was carried out using a DuPont 951 TGA instrument at a heating rate of 10°C/min under a N_2 atmosphere.

Synthesis of Polyurethane Macroiniferter (PUMI)

Isocyanate end-capped prepolymer based on PTMG-1000 (10.00 g, 0.01 M) and TDI (3.48 g, 0.02 M) was prepared at 70°C. When the isocyanate content reached half of the initial value as determined by dibutylamine titration, the contents of the reaction mixture were cooled to room temperature and chain extended using TPED (3.66 g, 0.01 M) in methyl ethyl ketone using DBTDL as a catalyst. The reaction was performed under nitrogen atmosphere. After 24 hours the PUMI so obtained was precipitated by pouring into a tenfold excess of methanol, filtered, dried, and stored at 0–4°C until use.

Synthesis of PU–PVP Multiblock Copolymers

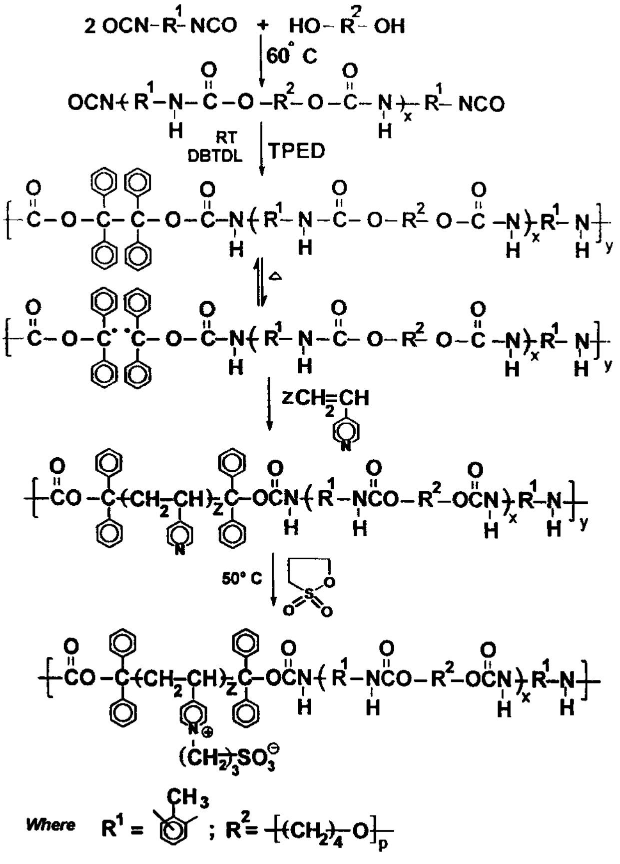
Required amounts of 4VP, PUMI, and *N,N'*-dimethylformamide were charged into cylindrical Pyrex tubes degassed by three alternate freeze–pump–thaw cycles, sealed under vacuum, and placed in a thermostated shaking water bath maintained at 70°C for selected times. After the stipulated time the reactions were arrested in an ice–salt mixture. The resulting solutions were poured into a tenfold excess of distilled water, filtered, washed thoroughly with methanol to extract the homopoly(4-vinylpyridine), dried, and weighed.

Conversion of PU–PVP Multiblock Copolymers into Their Zwitterionomers

The above-mentioned multiblock copolymers obtained (cf. Table 1) were dissolved in DMF and were reacted with an excess of γ-propane sultone at 50°C for 48 hours. The zwitterionomers were precipitated using a tenfold excess of diethyl ether, filtered, and dried in vacuo.

RESULTS AND DISCUSSION

Scheme 1 gives a detailed synthetic route for the synthesis of the multiblock copolymers. In macroiniferters, the initiating groups can be introduced (a) at one end of each polymer chain, (b) at both ends of each polymer chain, (c) between polymer blocks, and (d) as the side chains in the polymer. When these types (viz., a, b, c, and d) are decomposed in the presence of vinyl monomers, diblock, triblock, multiblock, and graft copolymers are formed, respectively. Since tetraphenylethane groups are separated by polyurethane blocks, the polyurethane macroiniferter when



SCHEME 1.

decomposed in the presence of vinyl monomers results in multiblock copolymer formation. As shown in Scheme 1, the central ethane bonds of tetraphenylethane moieties in the macroiniferter undergoes reversible homolytic cleavage and incorporates 4VP into the polyurethane.

Table 1 gives the results of block copolymerization of 4VP using PUMI. Figure 1 gives the time-conversion and time-$\overline{M}_n$ plots for the block copolymerization of 4VP using PUMI. As the polymerization time increases, both conversion (calculated in three different ways as given in Table 1) and $\overline{M}_n$ increased. This is a very typical result of "living" radical polymerization. Figure 2 gives conversion (R in Table 1)-$\overline{M}_n$ plot for the block copolymerization of 4VP. As the conversion increases, the $\overline{M}_n$ of the block copolymers also increases. This again is a typical result of "living" radical polymerization. In GPC analysis, unimodal peaks were observed; the curves shifting toward lower elution time as the polymerization time increases, showing an increase in molecular weight with an increase in polymerization time.

Figure 3 shows the ^{1}H-NMR spectrum of PU-PVP multiblock copolymer (cf. Table 1 obtained at 48 hours). The urethane protons of the polyurethane block resonate at about 8.1, 8.8, and 9.5 ppm. Since TDI used was a mixture of 2,4- and 2,6-isomers, the $-CH_3$ protons of TDI units are observed as a doublet at 2.0 and 2.1 ppm. The peaks corresponding to aromatic protons from the TPED, TDI, and 4VP units are observed between 6 to 7.5 ppm. The aliphatic protons of PTMG unit present in the $-CH_2$, $-O-CH_2$, and $-CH_2$ groups adjacent to the 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

TABLE 1. Block Copolymerization of 4VP with PUMI at 70°C in DMF[a]

No.	Time, hours	Conversion %			GPC results[b]		
		Q^c	R^d	S^e	$\overline{M}_n \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
1	0	12.95	–	–	5.16	10.01	1.94
2	3	13.12	4.27	32.53	6.12	11.93	1.95
3	9	14.27	5.33	37.34	6.63	13.13	1.98
4	24	18.23	7.94	43.57	7.93	15.62	1.97
5	48	22.24	11.02	49.56	8.48	16.28	1.92

[a] $[4VP]_0 = 2.0$ mol/L; $[PUMI]_0 = 3.125$ g/dL.

[b] After extraction of homopoly(4-vinylpyridine) using methanol; the value at 0 time is for PUMI.

[c] $$Q = \frac{\text{Weight of PU-PVP multiblock copolymers before extraction of homopolymers} \times 100}{\text{Initial weight of PUMI and 4VP taken}}$$

[d] $$R = \frac{\text{Weight of PU-PVP multiblock copolymers after extraction of homopolymers} \times 100}{\text{Initial weight of PUMI and 4VP taken}}$$

[e] $$S = \frac{\text{Weight of PU-PVP multiblock copolymers after extraction of homopolymers} \times 100}{\text{Weight of PU-PVP multiblock copolymers before extraction of homopolymers}}$$

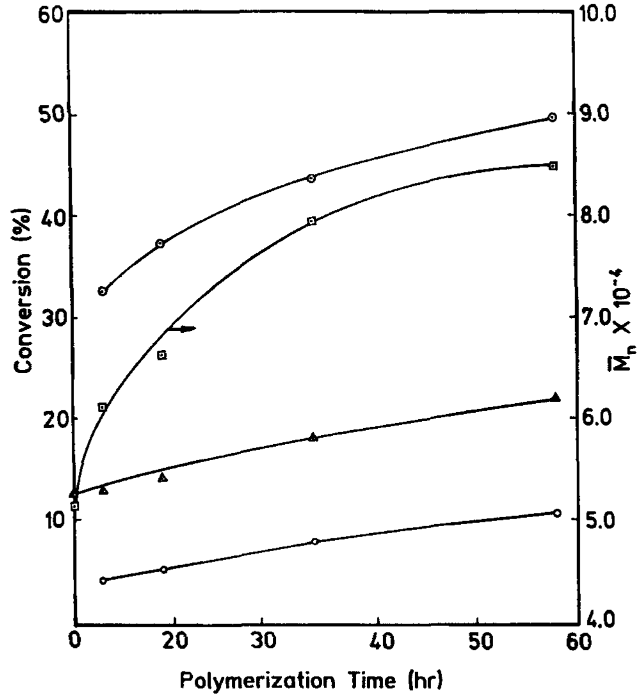


FIG. 1. Time-conversion [Q(△), R(○), and S(⊙) from Table 1] and time-$\bar{M}_n$ (⊡) relations for the polymerization of 4VP by PUMI in DMF at 70°C; $[PUMI]_0$ = 3.125 wt%; $[4VP]_0$ = 2.0 mol·L^{-1}.

the peak here. The $-CH_2$ and $-CH$ protons of the 4VP backbone resonate at 1.2 and 3.4 ppm, respectively. These peaks merge with the $-CH_2$ and $-O-CH_2$ peaks of the PTMG segment at 1.5 and 3.3 ppm, respectively. On conversion of the multiblock copolymer into the corresponding zwitterionomer, it was rendered insoluble even in highly polar solvents like DMSO. Therefore, the NMR spectrum of the zwitterionomer could not be recorded.

FT-IR spectra of polurethane iniferters show the presence of characteristic peak at about 1700 cm^{-1}, corresponding to carbonyl stretching of urethane groups. The N—H stretching vibration was observed at about 3300 cm^{-1}. The peak for aliphatic $-CH_2$ stretching vibrations was observed at 2900 cm^{-1}. The band due to C—N stretching and N—H deformations was observed at 1531 cm^{-1}. All these characteristic peaks were also present in the PU-PVP (cf. Table 1 obtained at 48 hours) multiblock copolymer. In addition, the intensity of the band at 1600 cm^{-1} due to C=C stretching of the aromatic groups increased because of the incorporation of vinylpyridinium moieties into the multiblock copolymer. In the case of the multiblock copolymeric zwitterionomers, in addition to all the above peaks, a new peak was observed at 1197 cm^{-1} due to S=O stretching, which confirms the conversion of PU-PVP multiblock copolymers into their corresponding zwitterionomers.

Figure 4 shows the TGA curves of PUMI, PU-PVP (cf. Table 1 at 48 hours),

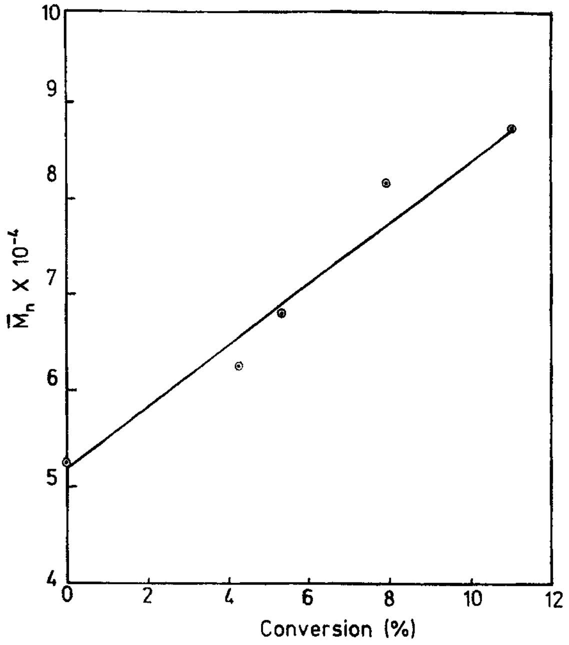


FIG. 2. Conversion-$\overline{M}_n$ plot for the polymerization of 4VP by PUMI in DMF at 70°C; $[\mathrm{PUMI}]_0 = 3.125$ wt%; $[\mathrm{4VP}]_0 = 2.0\ \mathrm{mol \cdot l^{-1}}$.

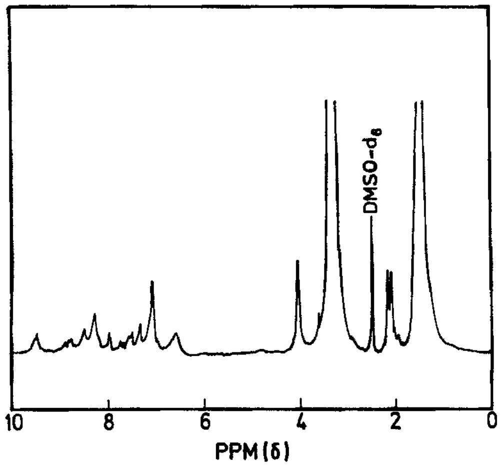


FIG. 3. ^{1}H-FT-NMR spectrum of PU-PVP multiblock copolymer.

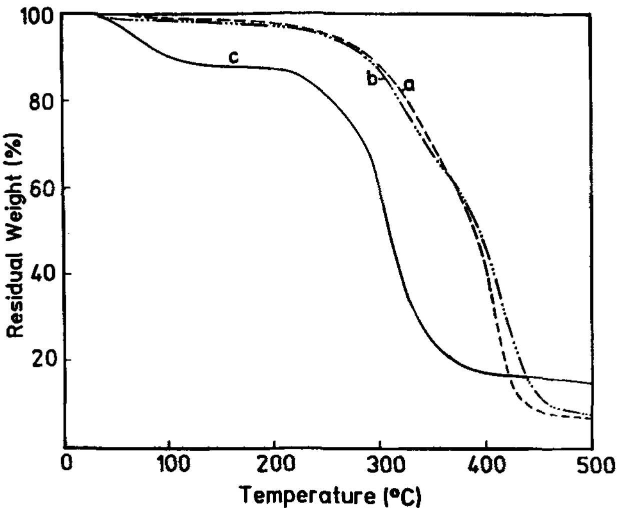


FIG. 4. TGA curves of (a) PUMI, (b) PU-PVP, and (c) zwitterionomer of PU-PVP.

and its corresponding zwitterionomer. The decomposition of the polyurethanes when viewed as a whole is a complex process to follow. The multistage decomposition observed for PU-PVP is due to the scission of chemically different segments in the polymer chain. Polyurethanes with high amount of aromatic moieties are relatively thermally more stable than those based on aliphatic diisocyanates. But very high thermal stability is not observed since the inherent cleavage of the urethane groups at around 230°C. The zwitterionomers were found to be less stable in the initial stages due to the moisture absorbed by the ionomers as the compounds are highly hygroscopic.

Figure 5 shows the DSC curves of the PUMI, PU-PVP (cf. Table 1 at 48 hours), and its corresponding zwitterionomer. The polymers were subjected to DSC scans in the temperature range of -100°C to $+120$°C under nitrogen atmosphere. The T_gs corresponding to the polyurethane blocks were below room temperature, which is characteristic of these polyurethane materials. As the ionic groups are incorporated in the polymer matrix, the T_g of the polyol unit shifted toward lower values. This is attributed to realignment of forces in the chain so that due to segmental incompatibility, phase separation takes place. In an earlier study on polyurethane cationomers and zwitterionomers based on pyridinium units, with an increase in the percentage of quaternization of the pyridinium sites, there was a progressive shift in the T_g to lower values [51, 52]. On comparing T_g of PUMI and PU-PVP (cf. Table 1 at 48 hours), the latter was higher than the former due to increased mixing of the soft and the hard segments (comprised of TDI, TPED, and the PVP block). The introduction of ionic groups into the block copolymer alters the hydrogen bonding of the polyurethane chains, leading to more phase purity such that the T_g of the polyurethane shifts toward that of the basic polyol unit. The conversion of the multiblock copolymer into its corresponding zwitterionomer is accompanied by a lowering in T_g by about 30°C.

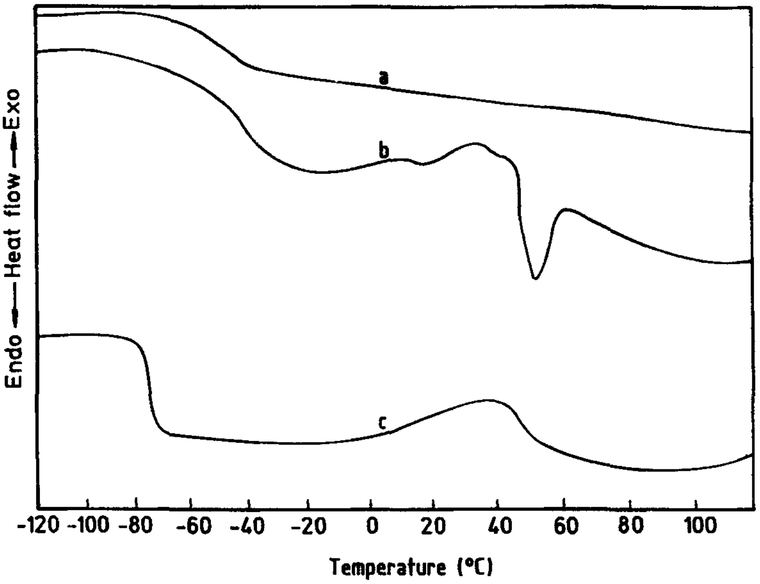


FIG. 5. DSC curves of (a) PUMI, (b) PU-PVP, and (c) zwitterionomer of PU-PVP.

CONCLUSIONS

PU-PVP multiblock copolymers have been prepared by "living" radical polymerization. The conversion and $\overline{M}_n$ increase with increasing polymerization time. This third method of synthesis of polyurethane ionomers by postpolymerization of macroiniferters offers the introduction of potential ionic moieties of different block lengths in between polyurethane blocks by just varying the polymerization time. The structures of the multiblock copolymers and the multiblock copolymeric zwitterionomers have been confirmed by using FT-NMR and FT-IR. DSC analyses were performed on the multiblock copolymers and the ionomers in the low temperature region to study the changes accompanying block copolymerization and conversion to the zwitterionomer.

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