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Preparation and characterization of novel thermoplastic elastomers by step/chain transformation polymerization

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Abstract

Three kinds of polyurethane–polyvinyl thermoplastic elastomers were synthesized by the combination of a two-step synthesis and chain polymerization. Their structures were confirmed by FT-IR and ^{1}H NMR, and their properties were also characterized. X-ray diffraction studies showed semicrystalline patterns for this type of copolymers. Tensile properties indicated that the copolymers had smaller extensibilities than typical polyurethanes. Thermogravimetric analysis curves displayed a better thermal stability for the copolymers due to their longer hard segments and the 1,1,2,2-tetraphenyl-1,2-ethanediol component. Differential scanning calorimetry studies and dynamic mechanical analysis revealed that this type of copolymers had microphase-separated structures and possessed elastomeric properties. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethane–polyvinyl thermoplastic elastomers; 1,1,2,2-Tetraphenyl-1,2-ethanediol; Microphase-separated structures

1. Introduction

Synthesis of thermoplastic elastomers is one of the prospective trends in macromolecular engineering. Elastomeric thermoplastic block copolymers are typically microphase-separation materials containing two types of segments in their molecular architecture. Compositional variables are known to affect the degree of phase segregation, phase mixing, and hard-segment domain organization, and accordingly the polymer properties [1,2].

Thermoplastic polyurethanes (PUs) are a class of high performance materials for versatile end use. However, preparation of typical PUs usually consists of a two-step synthesis method [3,4] and the monomers used are often restricted to difunctional compounds. Transformation reactions extend the range of possible monomer combinations in block copolymers [5–11]. This approach allows polymers produced by one type of polymerization to be terminally functionalized by groups capable of initiating a different mode of polymerization.

During the last decade, Ostu et al. had shown that the iniferter method could be used in the preparation of block copolymers [12]. In this concept, iniferters were used to design the structure of polymer chain ends in radical polymerization. Recently, polymethacrylic acid and polymethyl methacrylate prepared with the PU iniferter have been reported [13,14]. However, much information about the physical properties of this type of copolymers has not been mentioned.

On the basis of this approach, this article deals with the possibility of the synthesis of a new type of thermoplastic elastomer using a free-radical initiator 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED) which contains a well-known iniferter group (tetraphenylethane) to form a PU iniferter for the preparation of PU–polyvinyl block copolymers. Three kinds of monomers, i.e. acrylonitrile, methyl methacrylate, and styrene were used to form the polyvinyl segments. The three kinds of PU–polyvinyl copolymers were then characterized to determine their physical properties and morphology.

2. Experimental

2.1. Materials

4,4′-Methylene bis(4-phenylisocyanate) (MDI, Du Pont, Inc.), methyl isobutyl ketone (MIBK, Hayashi Chemicals), dimethyl formamide (DMF, Tokyo Chemicals), dimethyl sufloxide (DMSO, Nacalai Tesque, Inc.), styrene (St, Tokyo Chemicals), methyl methacrylate (MMA, Tokyo Chemicals), acrylonitrile (AN, Janssen Chimica) were distilled under reduced pressure. Dibutyltin dilaurate

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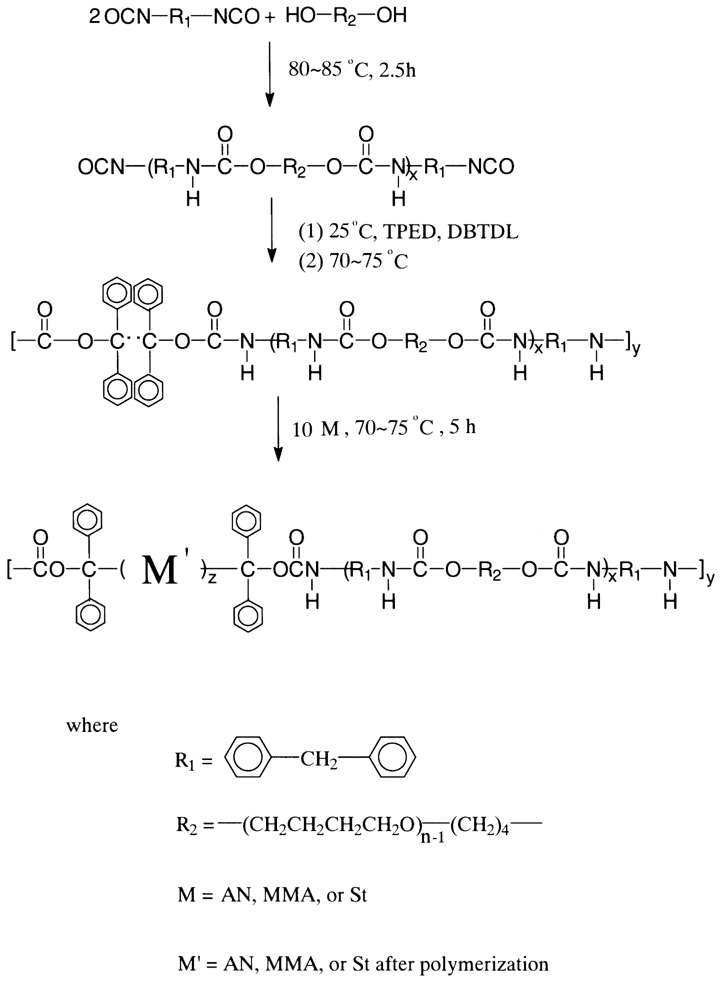

Scheme 1.

(DBTDL, Tokyo Chemicals), *N*-methyl-2-pyrrolidone (NMP, Bona Pure Chem. Co.), benzophenone (Ferak Berlin), isopropyl alcohol, chloroform, toluene, and tetrahydrofuran (THF) from Tokyo Chemicals were used as received. Polytetramethylene ether glycol (PTMG, Du Pont, Inc.) with molecular weight ($\overline{M}_n = 1000$) was degassed under vacuum at 55°C at 600 Pa (4.5 mmHg) for 3 h to remove any absorbed water. TPED was prepared from benzophenone and 2-propanol using the known method [15].

2.2. Synthesis of the polyurethane macroinitiator

Isocyanate terminated prepolymer was prepared by reacting 0.02 mol of MDI and 0.01 mol of PTMG in 70 ml DMF at 80–85°C for 2.5 h. This solution was then chain extended with 0.01 mol of TPED (in 15 ml DMF) solution at room temperature using DBTDL as a catalyst to obtain the PU macroiniferter.

2.3. Synthesis of PU–polyvinyl block copolyurethanes

To the above solution was added 0.1 mol of acrylonitrile and stirred at 70–75°C for 5 h. The viscous solution was poured into water to isolate the polymer. THF was used to extract homo-PAN and PU from the block copolymer. Conversion was about 58% after extraction. For convenience, this polymer was designated as PU–PAN. The PU–PS and PU–PMMA copolymers were prepared in a similar manner. Their conversions were also around 60%.

2.4. Characterization

Infrared (IR) spectra of the thin polymer films were obtained using a Bio-Rad FTS 165 Fourier transform infrared (FT-IR) spectrometer. The spectra were obtained over the frequency range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

The PU–polyvinyl block copolymers were dissolved in deuterium DMF (d-DMF), and then characterized with ^1H NMR using a Varian VXR 300S FT-NMR spectrometer. Qualitative solubility was determined using 0.01 g of polymer in 2 ml of solvent. Inherent viscosity (η_{inh}) measurements were determined at a solution concentration of 0.5 g polymer per 100 ml of solvent at 30°C using a

Table 1
Properties of PU–polyvinyl copolymers

Sample	η_{inh} (dl/g)[a]	Water content (%)	$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w}/\overline{M_n}$
PU–PAN	0.436	6.57	139 890	89 442	1.56
PU–PMMA	0.419	6.14	120 423	73 429	1.64
PU–PS	0.381	2.67	111 257	63 745	1.75

[a] Inherent viscosity at 30°C in DMF.

Cannon–Fenske viscosimeter. The water uptakes of the copolymers were measured from a weight increase after immersing the specimens in deionized water for 48 h at room temperature. Number average ($\overline{M_n}$), weight average ($\overline{M_w}$) molecular weights and molecular weight distribution (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 three μ-Styragel columns.

Wide-angle X-ray diffractograms (WAXD) were obtained on a Rigaku Geiger Flex D-Max III, using Ni-filtered CuK$_\alpha$ radiation (40 kV, 15 mA); the scanning rate was 4°/min. Measurements were performed with film specimens of about 0.1 mm thickness.

Stress–strain data of urethane copolymers were obtained using a Universal Testing Machine (Shimadzu AGS-500A Series) with a 10 kg load cell and film grips. The crosshead speed was 50 mm/min. Measurements were made at room temperature using a $1.2 \times 0.4\ \mathrm{cm}^2$ dumbbell sample.

Thermogravimetric analysis (TGA) experiments of the urethane copolymers were carried out on films placed in a platinum sample pan using a TA Instruments SDT-2960 analyzer. Sample films ranging from 4–5 mg were cut into small pieces and loaded into the platinum pan and sealed in the sample chamber. The samples were heated from 50 to 700°C under a nitrogen atmosphere and in static air at the rate of 10°C/min.

Differential scanning calorimetry (DSC) thermograms from −130 to 170°C were obtained using a TA Instruments DSC 2010 analyzer at a heating rate of 20°C/min under a dry nitrogen purge. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA 2980 unit with an operating temperature range from −150 to 150°C. The heating rate was set at 5°C/min. The sample size was approximately $60 \times 10 \times 2\ \mathrm{mm}^3$.

Table 2
Solubility of PU–polyvinyl copolymer (a scale for the different degrees of solubility is assigned as follows: 0, insoluble; 1, swell; 2, slightly soluble when hot; 3, soluble when hot, precipitate when cold; 4, soluble hot; and 5, soluble cold)

Polymer	Solvent						
	DMF	NMP	DMSO	$CHCl_3$	MIBK	THF	Toluene
PU–PAN	5	5	4	2	1	1	0
PU–PMMA	5	5	3	0	1	1	1
PU–PS	5	5	0	0	0	1	1

3. Results and discussion

3.1. Polymer synthesis

A three-step solution polymerization method derived from the conventional prepolymer technique was used for the preparation of PU–polyvinyl block copolymers. Novel polyurethane iniferter was synthesized by a step-type polymerization via the first two steps of this method. This iniferter was used to polymerize vinyl monomers through free radical mechanism. This macroiniferter yields three kinds of PU–polyvinyl multi-block copolymers in the presence of styrene, methyl methacrylate and acrylonitrile monomers as given in Scheme 1. If the reactions were ended in the first two steps, a typical PU elastomer with PTMG as the soft segment and MDI–TPED as the hard segment was synthesized. However, if a vinyl monomer such as AN was added, the hard-segment component was changed. It has been indicated that conversion, $\overline{M_n}$ and inherent viscosity increased with increasing monomer concentrations at constant polymerization time and PU macroiniferter, while increased polymerization time conversion, $\overline{M_n}$ and inherent viscosity also increased [16]. Hence, molecular weights of polymers increase with increasing monomer concentrations at constant polymerization time. Since the hard-segment length was controlled by the ratio of vinyl monomers added, the effect of vinyl monomers was manifested by a vinyl monomer/PTMG mole ratio of 10/1 during the synthesis.

An interesting phenomenon had been observed when the step/chain transformation polymerization occurred. The reactions of PU iniferters were light yellow originally. Upon addition of vinyl monomers, the reactions turned clear, indicating the formation of polymer radicals.

The inherent viscosity, water uptake, and GPC results of the synthesized elastomers are shown in Table 1. In comparison with the water uptake (ca. 2%) of typical PUs, the higher water uptakes for PU–PAN and PU–PMMA suggest that longer and more polar hard segments increase the hydrophilic character of elastomers.

Qualitative solubility of PU–polyvinyl polymers in various solvents is shown in Table 2. These samples are

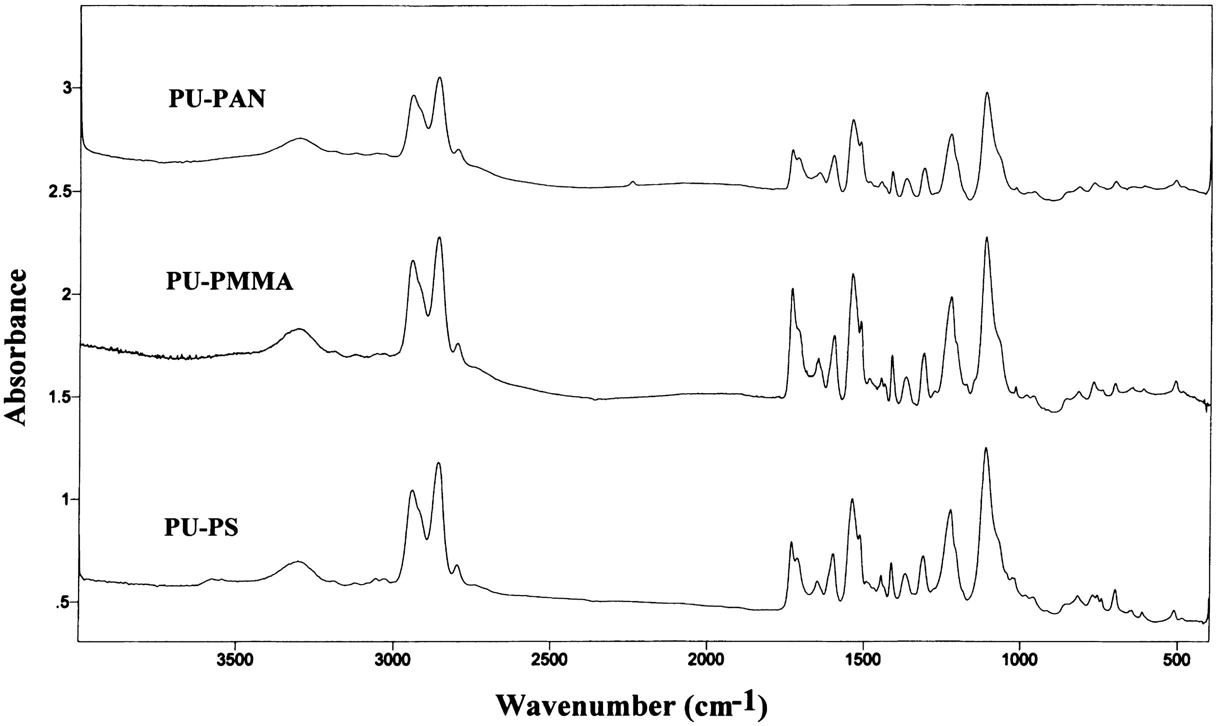

Fig. 1. IR spectra of PU–polyvinyl copolymers.

soluble in aprotic polar solvents such as DMF and NMP, and insoluble in common organic solvents.

3.2. IR characterization

IR spectra of three kinds of PU–polyvinyl polymers are illustrated in Fig. 1. It is noted that the incorporation of PAN into the urethane copolymer was evidenced by the appearance of the $-C\equiv N$ absorption band at 2244 cm^{-1}. The other absorption bands show the characteristic absorptions of typical PUs. The major NH band appears at 3300 cm^{-1} and is attributed to the N–H band which is hydrogen bonded. The carbonyl absorptions in the urethane groups split into two peaks at 1732 and 1712 cm^{-1} which can be assigned to free and hydrogen bonded urethane carbonyl groups. In the PU–PS copolymer, the most dramatic difference with the spectrum mentioned above is the appearance of the band around 3030–3080 cm^{-1} which is assigned to the C–H stretch of aromatic ring. Other key features such as the absorption bands at 730–770 cm^{-1} and 698 cm^{-1} also show characteristic absorptions of typical aromatic rings with five adjacent free hydrogen atoms. Nonetheless, the absorption bands in the IR spectra of PU–PAN and PU–PMMA in this region look similar yet the two copolymers do not have absorption bands at 730–770 cm^{-1} and 698 cm^{-1}. This spectrum proves clearly that PU–PS has been successfully synthesized. Subsequently, as compared to PU–PS and PU–PAN, the IR spectrum of PU–PMMA clearly shows the increase of carbonyl absorption in 1731 cm^{-1}, indicating the PMMA segment being incorporated into the copolymer.

3.3. ^{1}H NMR Analysis

Fig. 2 shows the ^{1}H FT-NMR spectrum of PU–PAN block copolymer. The peaks at about 8.55 and 9.38 ppm are due to the N–H protons of urethane linkages. The peak corresponding to aromatic protons from TPED and MDI units are observed between 7 and 7.5 ppm. The aliphatic protons of PTMG unit existing in the $-OCH_2C\underline{H}_2$, $-O-CH_2$ appear at about 1.59 and 3.39 ppm, respectively, whereas the $-O-CH_2$ adjacent to urethane groups are observed around 4.08–4.13 ppm. The presence of resonance peaks around 2.23 ppm is attributed to $N\equiv C-CH-$. The result confirms that the PAN block is incorporated in between PU block as given in Scheme 1. Next, the spectrum of PU–PS is characterized by the increase of the resonance peak around 7.08–7.18 ppm. The structure of PU–PMMA is evident by the presence of the resonance peak at 3.63 ppm representing $-COOCH_3$.

3.4. GPC Analysis

GPC results show that the PU macroiniferter initiates monomers polymerization. Preliminary experiments have shown that in this system both conversion and $\overline{M_n}$ increase with increasing polymerization time. Furthermore, the GPC traces for all of PU–polyvinyl block copolyurethanes show an increase in molecular weights, when compared to the PU

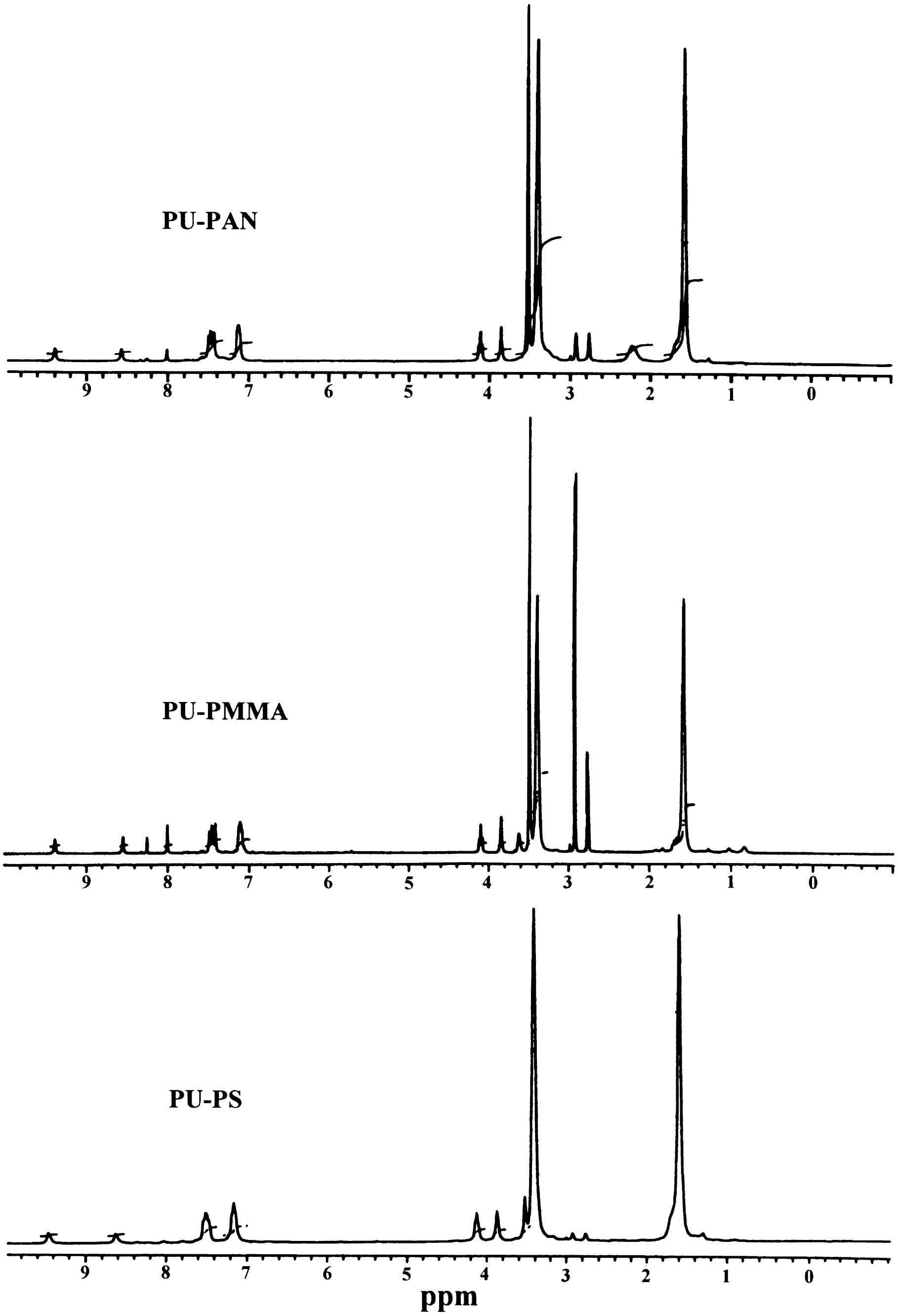

Fig. 2. ^{1}H NMR spectra of PU–polyvinyl copolymers.

iniferter. The above results indicate that a step/chain transformation polymerization reaction has occurred.

3.5. Wide-angle X-ray diffraction WAXD

Fig. 3 represents the WAXD curves of PU–polyvinyl copolymers. For the PU–PAN copolymer, the curve shows a small peak at $2\theta = 8.2°$ and a broad band split into a triplet at $2\theta = 17.0$, 19.2 and 20.4°, respectively. The curves for PU–PMMA and PU–PS show a somewhat similar contrast. The X-ray patterns for these samples indicate that the samples are semicrystalline materials. Since a broader peak indicates a lower crystallinity, the crystallinity of these materials can be ranked in the following order: PU–PS < PU–PAN < PU–PMMA as seen in Fig. 3. This may be due to the more hydrogen bondings of urethane carbonyls increase the crystallinity of the copolymer. This result is also confirmed by the tensile strength measurements, which will be discussed later.

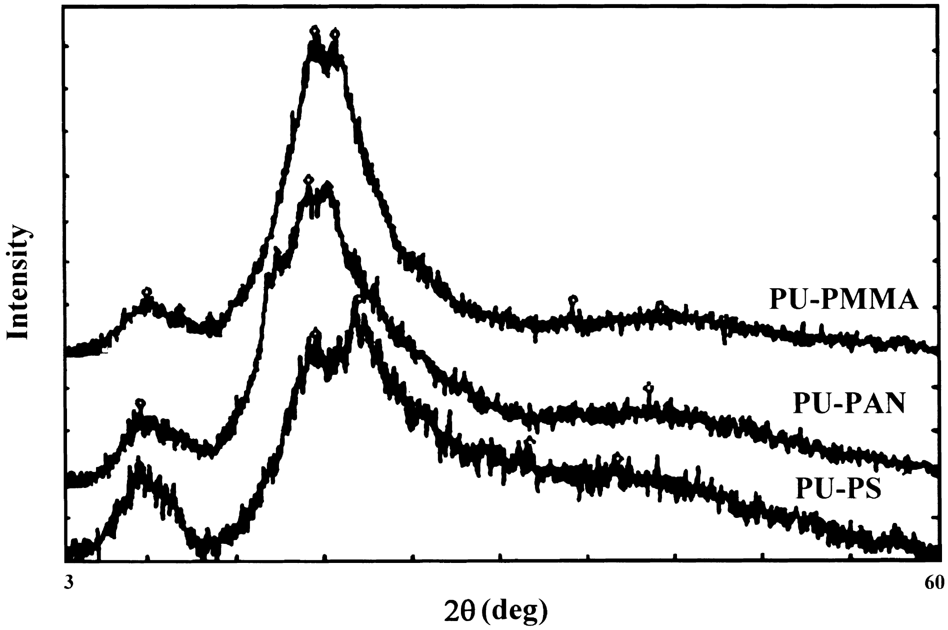

Fig. 3. X-ray diffractograms of PU–polyvinyl copolymers.

3.6. Tensile properties

The stress–strain curves for PU–polyvinyl copolymers are shown in Fig. 4. As compared to the hard segments of typical PUs, polyvinyl hard segments are more rigid and longer (due to the higher synthetic mole ratio). Hence, the new thermoplastic elastomers are more brittle and exhibit smaller extensibility than typical PUs. In contrast, higher tensile strength for PU–PMMA and PU–PAN may be attributed to the higher degrees of hydrogen bonding of urethane carbonyls in both samples as seen in the IR spectra of the samples. Conversely, a lower crystallinity for PU–PS may increase the extensibility of the copolymer.

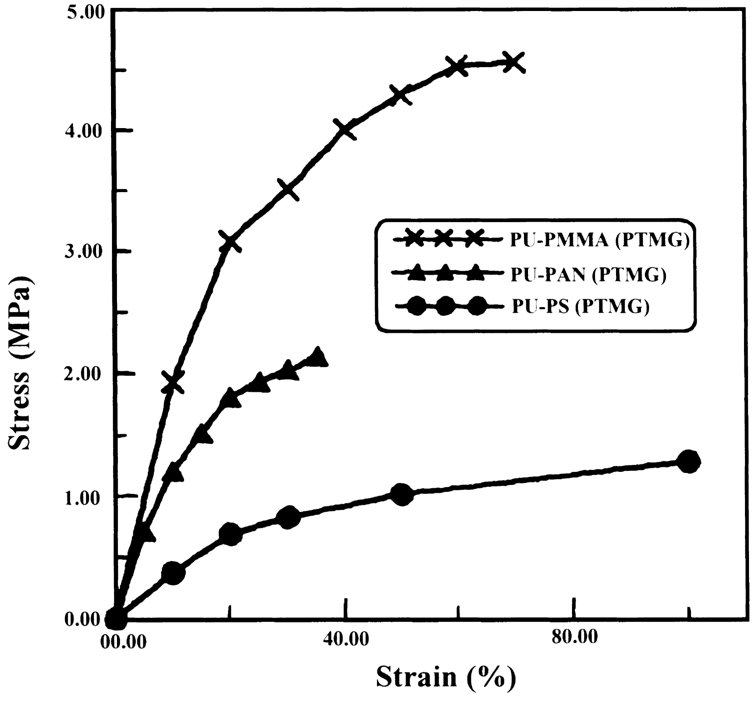

Fig. 4. Stress–strain curves for PU–polyvinyl copolymers.

3.7. Thermal analysis

The thermal stability for PU–polyvinyl materials in

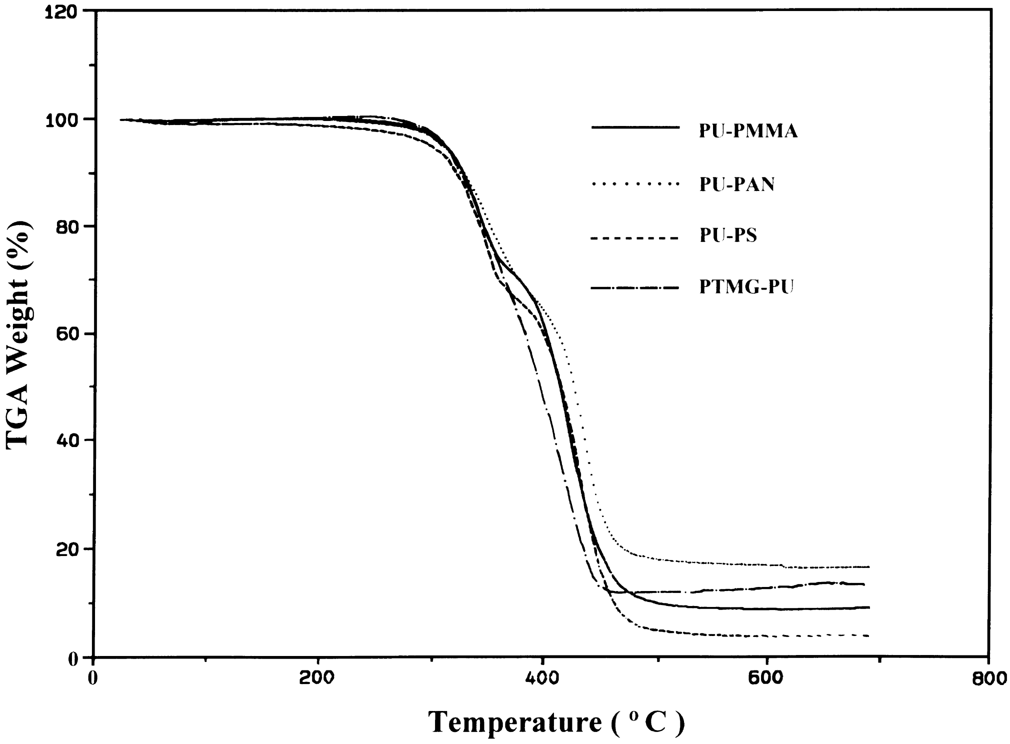

Fig. 5. TGA curves of PU–polyvinyl copolymers under a nitrogen atmosphere.

nitrogen is illustrated in Fig. 5. As seen in the figure, the TGA curves display a two-step mechanism for the degradation, which is quite different with the one-step degradation mechanism of typical PUs. In comparison with the one stage degradation of a typical polyurethane PTMG–PU (MDI reacted with PTMG ($\overline{M_n} = 1000$) and then chain extended with ethylene diamine), it is worth noting that $T_{50\%}$ (the temperature at which 50% weight loss has occurred) can

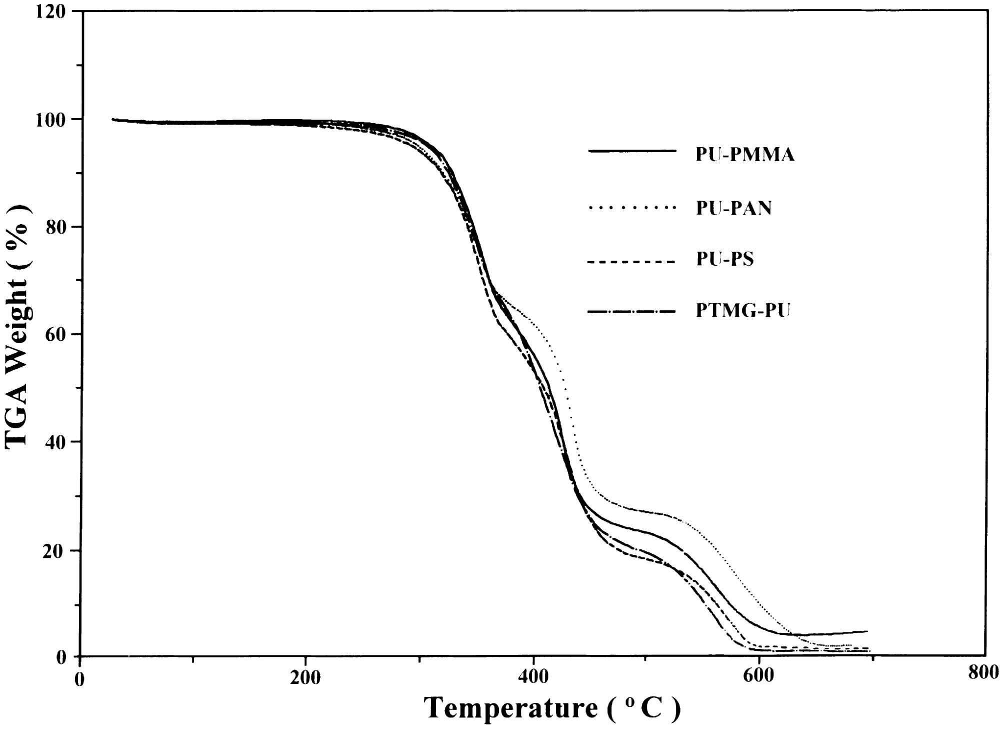

Fig. 6. TGA curves of PU–polyvinyl copolymers in static air.

Table 3
Characteristic temperatures on TGA curves

Sample	Degradation in nitrogen		Degradation in air	
	$T_{10\%}$	$T_{50\%}$	$T_{10\%}$	$T_{50\%}$
PU–PAN	328.6	425.0	317.2	425.0
PU–PMMA	328.6	412.5	325.0	410.7
PU–PS	321.4	413.8	316.1	405.8
PTMG–PU	326.8	395.6	321.4	401.8

be ranked in the following order: PTMG–PU < PU–PS ≅ PU–PMMA < PU–PAN according to their different hard-segment components. Since it has been indicated that the initial degradation occurs in the hard segments [17], this may imply that the hard segment which is composed of TPED with a polyvinyl segment has a different degradation mechanism with that of typical PUs. The initial degradation may arise from the polyvinyl segments while the degradation in the later stage may arise due to the TPED segments.

In comparison with the curves under a nitrogen stream, the TGA curves for the three copolymers show a quite different behavior in air. Fig. 6 clearly shows three stages of degradation for all of the samples and the temperatures of 10% weight loss are lower than those of the same samples degraded in nitrogen. This may be attributed to the fact that oxidation reactions occur in the soft and hard segments. Further, $T_{50\%}$ is also increasing in the order: PTMG–PU < PU–PS < PU–PMMA < PU–PAN as seen in the figure. The results are shown in Table 3. In the second stage, the degradation is caused by the soft segments as stated before, while in the third stage it is probably due to the oxidation reactions of the MDI and TPED components in the hard segments. Hence, the third stage degradation occurs and the rate of weight loss is reduced. The mechanisms of the degradation reactions are beyond the scope of this paper.

3.8. Differential scanning calorimetry

The DSC curves are shown in Fig. 7 for the as-cast materials. It is apparently seen that two distinct T_gs are presented in this picture for the three copolymers, the low temperature one represents the soft-segment T_g and the high temperature one denotes the hard-segment T_g. It testifies that they are microphase-separated thermoplastic elastomer materials.

3.9. Dynamic mechanical analysis

The dynamic mechanical properties of the PU–polyvinyl copolymers are shown in Figs. 8–10. The storage modulus (E') and dissipation factor (tan δ) of all of the three copolymers are generally characteristic of a system where a two-phase morphology is observed. Two transition temperatures are observed from the E' curves. The low temperature

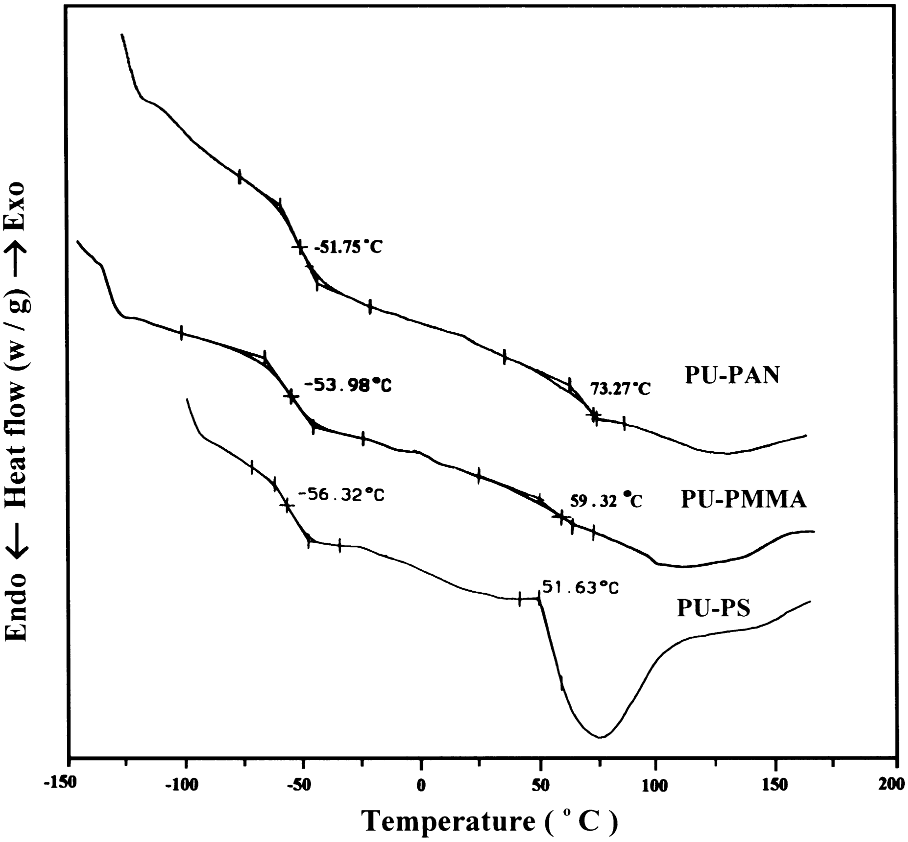

Fig. 7. DSC curves of PU–polyvinyl copolymers.

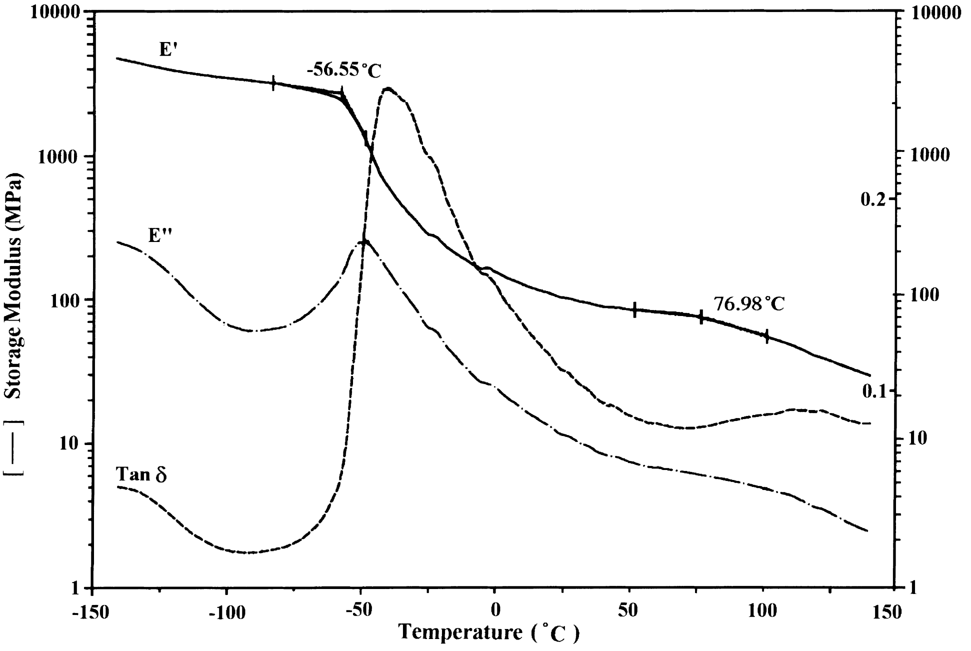

Fig. 8. Storage modulus (E'), loss modulus (E''), and tan δ curve for PU–PAN copolymer.

transition is related to the T_g of the soft-segment phase, while the high temperature transition correlates with the T_g of the hard-segment domains. It was reported that the soft-segment T_g in the two-phase system is a sensitive index of phase separation. As the degree of phase separation decreases, the T_g of the soft-segment phase increases. Hence, the degrees of phase separation of the three copolymers look similar because their T_gs are almost equal. These results are consistent with the DSC Data. On the other hand, the E' data also provide information on the mechanical behavior of the PU–polyvinyl copolymers. As seen from these figures, PU–PS is a softer material than PU–PMMA or PU–PAN.

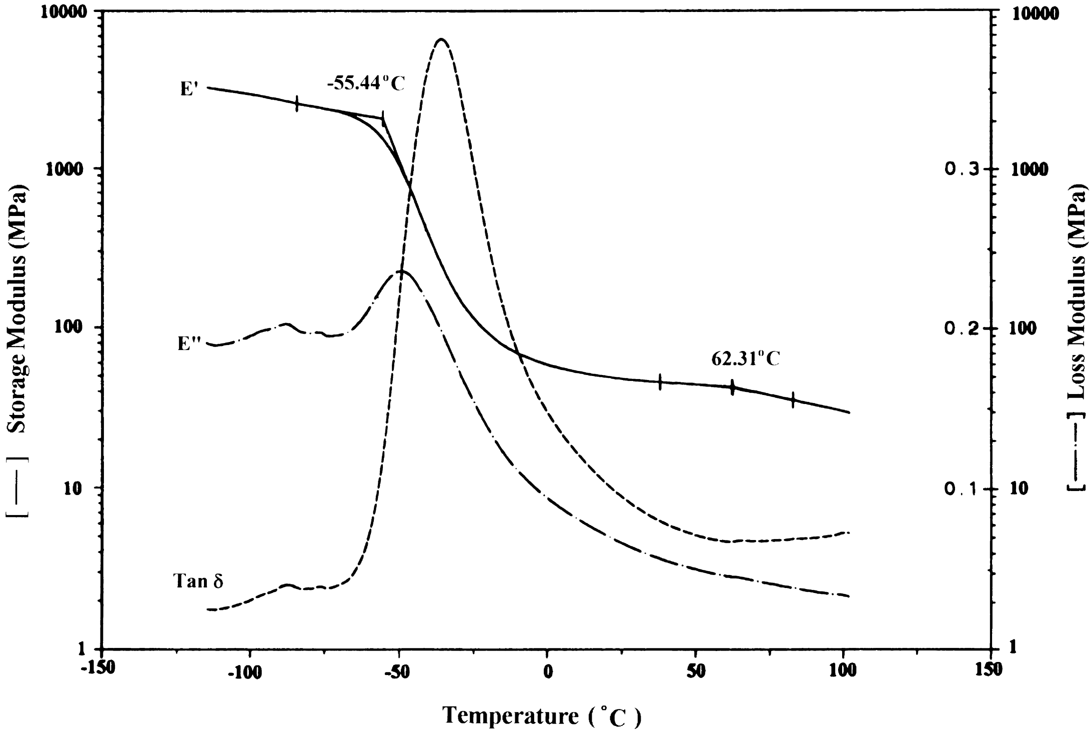

Fig. 9. Storage modulus (E'), loss modulus (E''), and tan δ curve for PU–PMMA copolymer.

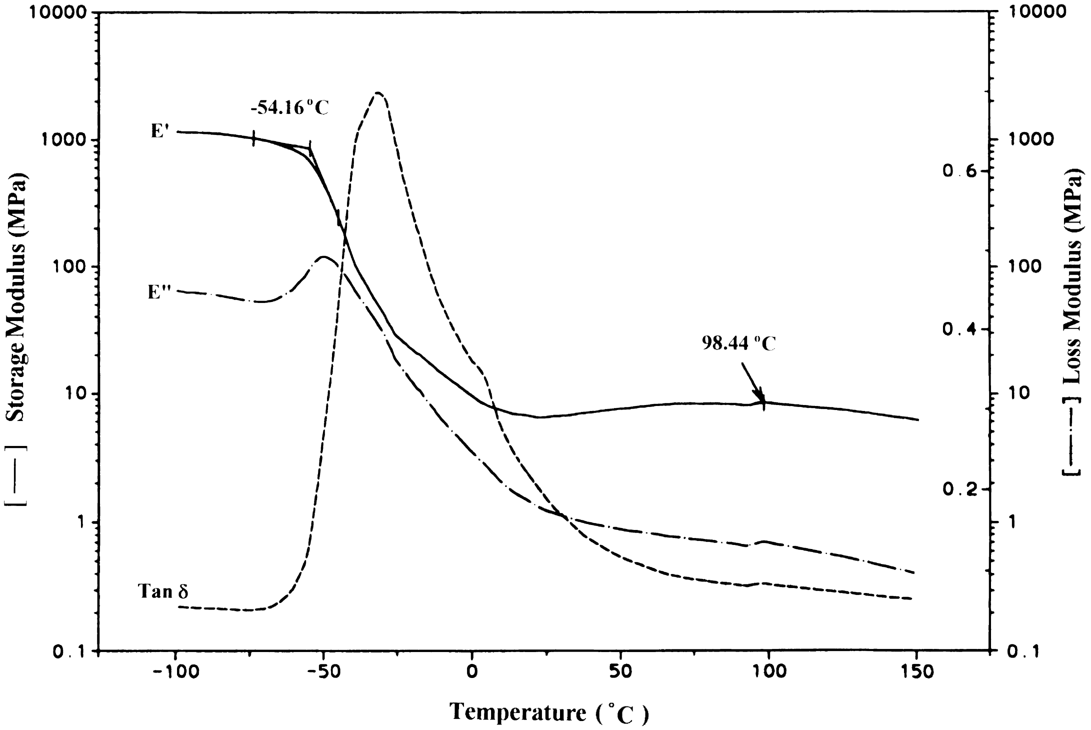

Fig. 10. Storage modulus (E'), loss modulus (E''), and tan δ curve for PU–PS copolymer.

4. Conclusions

Three kinds of PU–polyvinyl thermoplastic elastomers were synthesized from a PU iniferter. The TPED component and the polyvinyl segments were incorporated in following stages and formed the hard segments of the copolymers. These samples are semicrystalline materials due to the reason that their longer hard segments increase the crystallinity of the copolymers. Further, the TPED component and polyvinyl segments of the three copolymers result in different degradation mechanisms compared with typical PUs. DSC and DMA studies indicate that these samples are microphase-separated materials and exhibit elastomeric properties.

Acknowledgements

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