# AB Crosslinked Polymers Based on Cationomeric Polyurethane and Poly(methyl methacrylate): Static and Dynamic Mechanical Studies

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**ABSTRACT:** Vinyl-terminated polyurethane (VTPU) was prepared by end-functionalizing isocyanate-terminated prepolymers with 2-bromoethanol and subsequently quartenizing with 4-vinylpyridine. The vinyl functionality was then effectively utilized for preparing AB crosslinked polymers (ABCPs) with methyl methacrylate (MMA). ABCPs prepared with variable weight ratios on $PTMG_{1000}$-based VTPU/MMA (8/2, 6/4, 5/5, 4/6, 2/8) and those prepared at a 5/5 weight ratio with different polyols ($PTMG_{1000}$, $PPG_{1000}$, and $PCL_{1250}$) in VTPU were characterized by Fourier transform infrared spectroscopy (FTIR) and further analyzed for thermal and mechanical properties. FTIR spectral results confirm quartenization of heterocyclic nitrogen, leading to crosslinking. Thermogravimetric analyses show enhanced thermal stability of the crosslinked systems. The stress–strain measurements reveal increasing tensile strength with increasing amounts of MMA. Comparison of dynamic mechanical spectra of ABCPs based on $PTMG_{1000}$ shows that the 5/5 composition exhibits good damping over a broad temperature range. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 813–821, 2001

**Key words:** vinyl-terminated polyurethane; AB crosslinked polymers; quaternization; mechanical properties; damping.
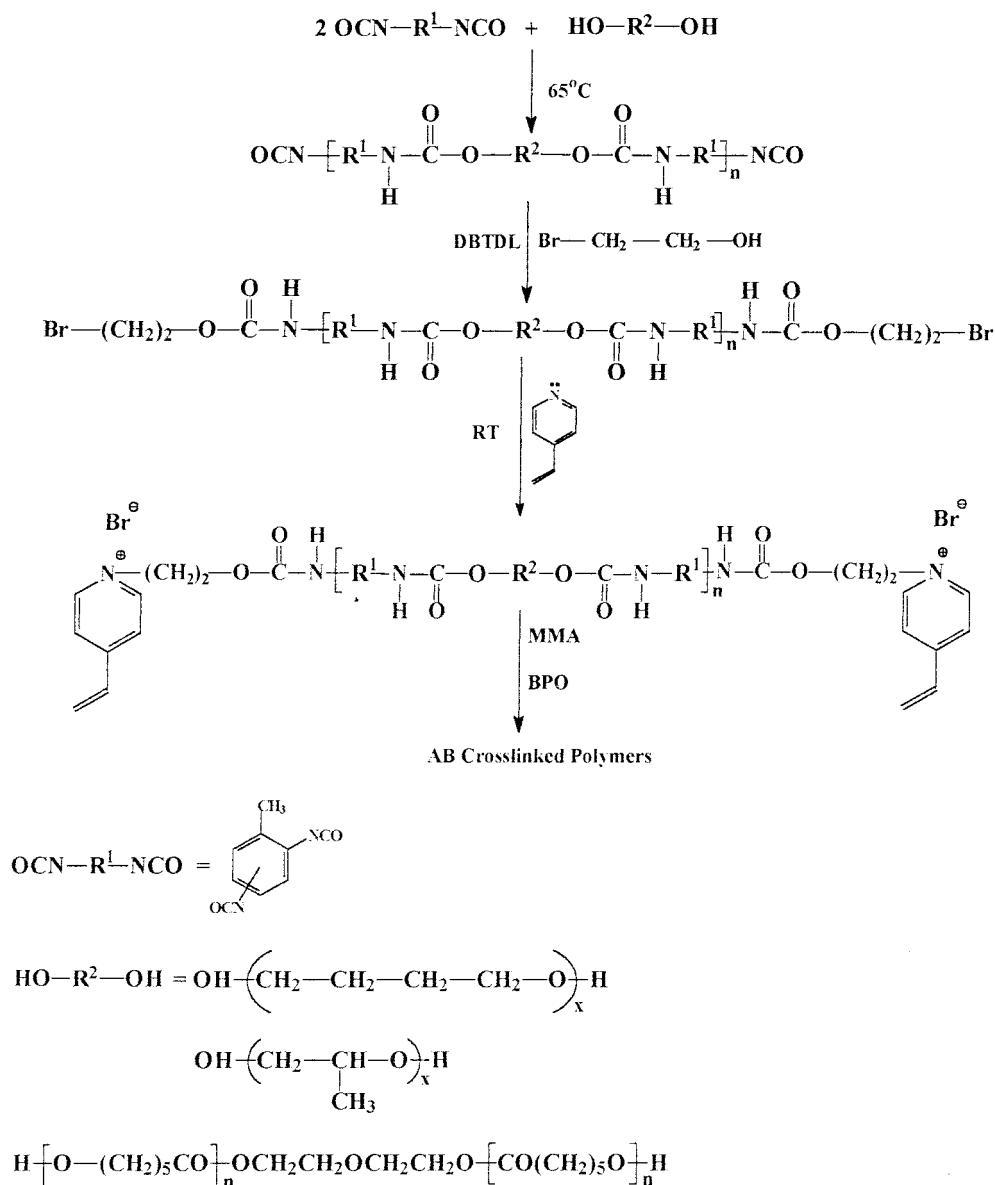
## INTRODUCTION

Two kinds of polymer molecules may be combined in many ways to produce interesting materials. Well-known examples include polymer blends,[1,2] graft copolymers,[3,4] block copolymers,[5] and AB crosslinked polymers.[6–13] The term AB crosslinked polymer (ABCP) refers to a polymer in which chains of polymer A are connected by long crosslinks of a chemically different polymer B at both ends or at various points along the chains.[7] ABCPs and interpenetrating polymer networks (IPNs) are crosslinked networks which are prepared with improved physical properties. Although both ABCPs and IPNs are crosslinked networks, the chemical structures of these networks are different: IPNs are unique blends of two crosslinked polymer networks containing no covalent bonds or grafts between networks, whereas a single network is generated in ABCP. Studies on ABCPs have been reported in many references.[10–14] These ABCPs or joined IPNs materials exhibited high damping over a broad temperature range and find application in controlling vibration and noise. Some thermoplastic materials have damping properties comparable to ABCPs, but have the disadvantage of flowing above their $T_g$ and, hence, cannot be used as engineering materials. ABCPs can overcome this disadvantage.[15–19]

$$2 \text{ OCN}-\text{R}^1-\text{NCO} \quad + \quad \text{HO}-\text{R}^2-\text{OH}$$

65°C

Scheme 1 reaction diagram.

$$\text{OCN}\left[\text{R}^1-\underset{H}{N}-\overset{O}{\underset{\|}{C}}-O-\text{R}^2-O-\overset{O}{\underset{\|}{C}}-\underset{H}{N}-\text{R}^1\right]_n \text{NCO}$$

DBTDL | Br—CH₂—CH₂—OH

$$\text{Br}-(\text{CH}_2)_2-O-\overset{O}{\underset{\|}{C}}-\underset{H}{N}\left[\text{R}^1-\underset{H}{N}-\overset{O}{\underset{\|}{C}}-O-\text{R}^2-O-\overset{H}{\underset{\|}{C}}-\underset{O}{N}-\text{R}^1\right]_n \underset{H}{N}-\overset{O}{\underset{\|}{C}}-O-(\text{CH}_2)_2-\text{Br}$$

RT

$$\text{AB Crosslinked Polymers}$$

MMA

BPO

$$\text{OCN}-\text{R}^1-\text{NCO} =$$

$$\text{HO}-\text{R}^2-\text{OH} = \text{OH}\left(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-O\right)_x \text{H}$$

$$\text{OH}\left(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-O\right)_x \text{H}$$

$$\text{H}\left[O-(\text{CH}_2)_5\text{CO}\right]_n \text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}\left[\text{CO}(\text{CH}_2)_5O\right]_n \text{H}$$

**Scheme 1**

Ionomers are polymers containing a small number of ionic groups (<10 mol %) in the polymer backbone. The presence of a small number of ionic groups in the hydrophobic polymer backbone leads to interesting properties of the material. Polyurethane (PU) ionomers have been synthesized predominantly by using an ionic diisocyanate or an ionic diol at the chain-extension stage and by postmodification of a preformed PU. In the former case, PU anionomers[20–27] (with carboxylic, sulfonic, and phosphoric acid groups), cationomers,[28–35] and zwitter ionomers[36–40] have been studied in great detail. Preparation of PU materials with a specific arrangement of ionic groups

have seldom been reported. To this effect, telechelic, that is, end-functional PU ionomers, would be of interest. Recently, telechelic PU cationomers containing end-functionalized 4-vinylpyridinium moieties were reported.[41] In this article, static and dynamic mechanical properties of AB-CPs from vinyl-terminated PU (VTPU) and methyl methacrylate (MMA) are reported.

## EXPERIMENTAL

### Materials

Poly(propylene oxide)glycol of molecular weight 1000 (PPG$_{1000}$), poly(tetramethylene oxide)glycol of

molecular weight 1000 ($PTMG_{1000}$), and polycaprolactone diol of molecular weight 1250 ($PCL_{1250}$) were received from Aldrich (Milwaukee, WI) and dried under a vacuum before use. Toluene diisocyanate (TDI; a mixture of 80% 2,4 and 20% 2,6 isomers) and dibutyltin dilaurate (DBTDL; Aldrich) were used as received. 2-Bromoethanol and 4-vinylpyridine (Lancaster, Lancashire, UK) were distilled and used. MMA (S.d. fine. Chem., Bombay, India) was washed with aqueous NaOH to remove the inhibitor, distilled under a vacuum, and stored at 0–4°C until use. Benzoyl peroxide (BPO) (S.d. fine. Chem.) was recrystallized from ethyl alcohol.

## Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Avatar 360 infrared spectrometer having an HATR accessory. Thermogravimetric analysis (TGA) was carried out using a DuPont 910 thermogravimetric analyzer at a heating rate of 20°C/min in a $N_2$ atmosphere (flow rate of 50 mL/min). Strips ($20 \times 10 \times 2.0$ mm$^3$) of each material were examined with a DMA 2980 dynamic mechanical analyzer (TA Instruments, USA) in the tensile mode (tension film) over the temperature range of −100 to +100°C at a heating rate of 5°C/min., a strain amplitude of 20 $\mu$m, and a frequency of 1 Hz. Samples for stress–strain analysis were cut at a geometry of 4.0 mm $\times$ 10.0 mm and kept for conditioning at a temperature of $20 \pm 2$°C and relative humidity of $65 \pm 2\%$ for 24 h before testing. The tensile testing was done using an Instron universal testing machine, Model 4501 at an elongation rate of 100 mm/min. The specimens conformed to the ASTM standard.

## Synthesis of VTPUs

Dried polyol was taken in a three-necked roundbottom flask, fitted with a mechanical stirrer, nitrogen inlet, and a dropping funnel, and heated in an oil bath. When the temperature reached 65°C,
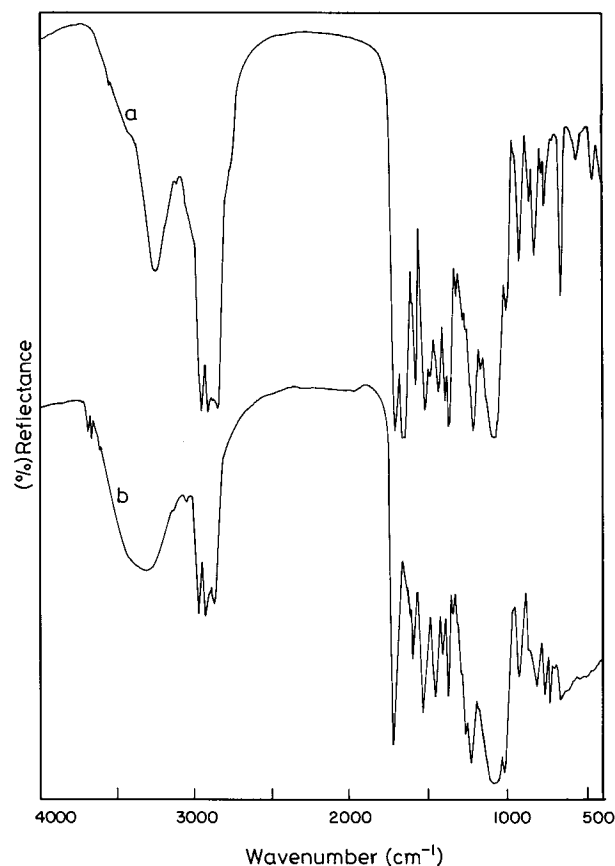
**Table I   Characteristics of ABCP Based on $PTMG_{1000}$ at 5/5 Composition**

| | |
|---|---|
| Tensile strength (MPa) | 4.9 |
| Elongation at break (%) | 429 |
| Tan $\delta_{max}$ | 0.64 |
| Temperature range (°C) | |
| (tan $\delta > 0.2$) | −29.4 to + 54.2 |



**Figure 1** (a) FTIR spectrum of $PTMG_{1000}$-based VTPU (5/5 composition). (b) FTIR spectrum of $PTMG_{1000}$-based VTPU (5/5 composition).

TDI was added drop by drop with stirring. The temperature was then increased to 70°C and the reaction was allowed to proceed until the isocyanate content reached half of the initial value (as determined by dibutylamine titration). 2-Bromoethanol was the added dropwise followed by the addition of DBTDL (1 mol % based on isocyanate content). After 3 h, the contents were cooled to room temperature, a stoichiometric amount of 4-vinylpyridine was added, and the mixture stirred for another 24 h at room temperature. The resulting VTPU was stored at 0–4°C until use.

## Synthesis of ABCP

Varying weight ratios (8/2, 6/4, 5/5, 4/6, 2/8) of VTPU and MMA were mixed homogeneously with a calculated amount of a free-radical initiator (BPO, 0.02% w/w) at room temperature. This mixture was injected into a glass mold and placed in a thermostated water bath at 75°C for 48 h. The resulting films were placed in a vacuum oven at
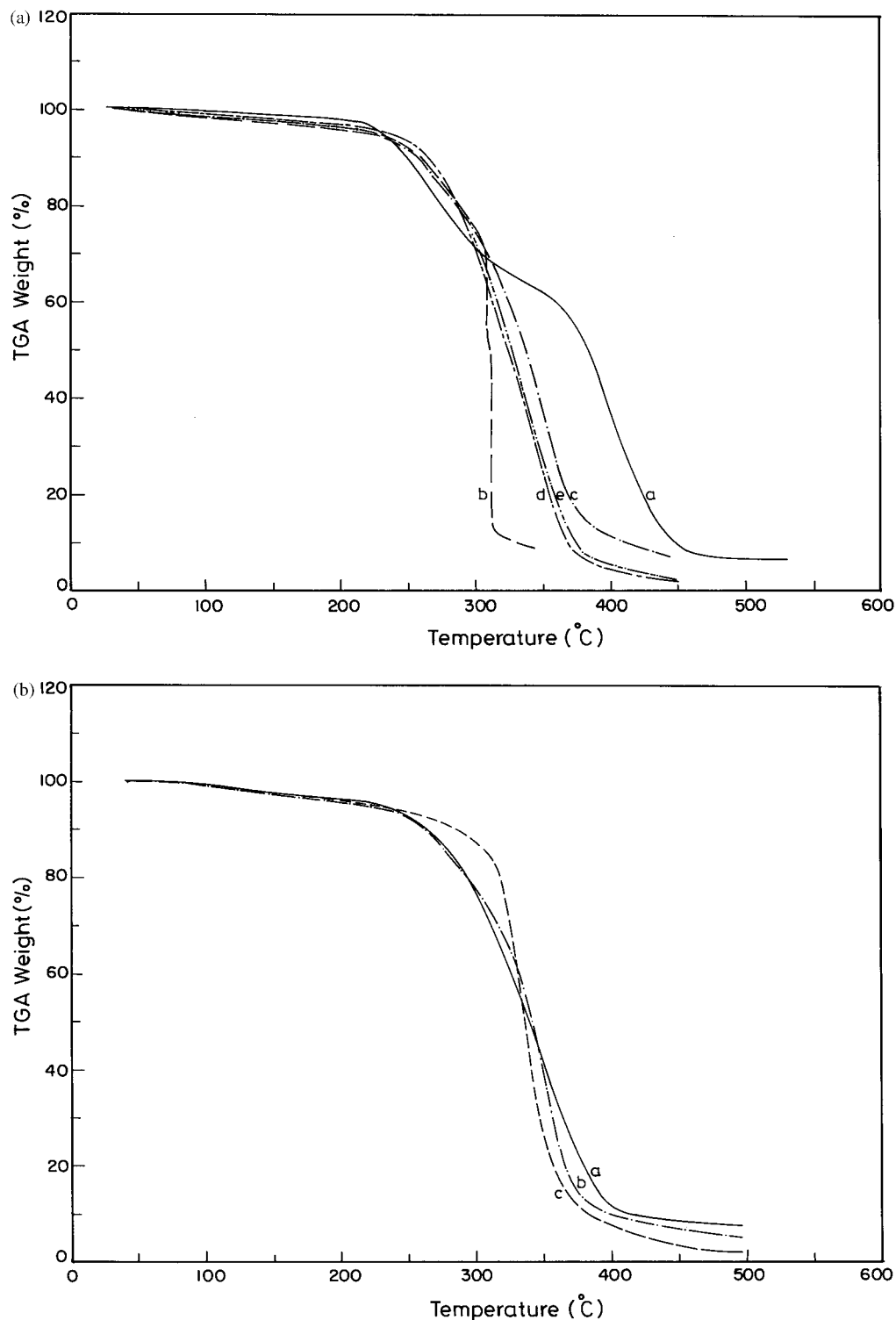
**Figure 2** (a) TGA thermograms of $PTMG_{1000}$-based ABCP [VTPU/MMA weight ratio = (a) 8/2, (b) 6/4, (c) 5/5, (d) 4/6, and (e) 2/8]. (b) TGA thermograms of ABCP [VTPU/MMA weight ratio = 5/5]: (a) $PPG_{1000}$; (b) $PTMG_{1000}$; (c) $PCL_{1250}$.
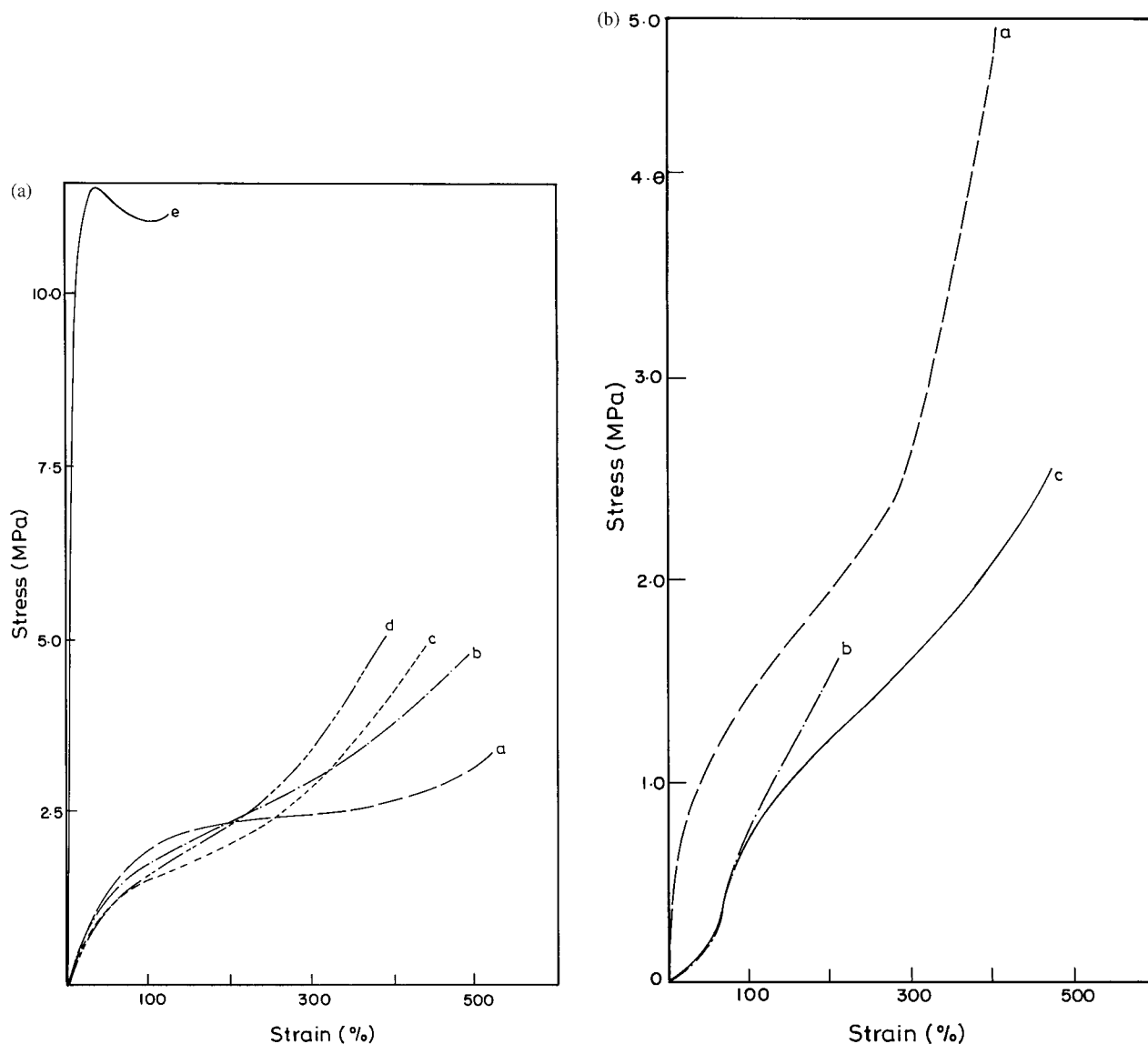
**Figure 3** (a) Stress–strain curves of $PTMG_{1000}$-based ABCP [VTPU/MMA weight ratio = (a) 8/2, (b) 6/4, (c) 5/5, (d) 4/6, and (e) 2/8]. (b) Stress–strain of ABCP [VTPU/MMA weight ratio = 5/5]: (a) $PPG_{1000}$; (b) $PTMG_{1000}$; (c) $PCL_{1250}$.

50°C for 48 h to remove unreacted monomers. The same procedure was adopted to prepare ABCPs of 5/5 composition with different polyols. The steps involved in the synthesis of ABCPs are represented in Scheme 1. The specimens, when kept immersed in dimethylformamide for a specific period of time, swelled but did not dissolve, thus confirming crosslinking.

## RESULTS AND DISCUSSION

The properties of ABCPs prepared with $PTMG_{1000}$-based VTPU and MMA monomer of 5/5 composi-

tion are shown in Table I. The composition exhibits good damping over a broad temperature range and shows better tensile properties.

**Infrared Spectroscopy**

The FTIR spectrum of VTPU based on $PTMG_{1000}$ (Fig. 1) shows characteristic peaks due to the urethane $>NH$ and $>C{=}O$ stretching at 3300 and 1725 $cm^{-1}$, respectively. The absorption with high intensity at 1680 $cm^{-1}$ corresponds to the vinyl $>C{=}C<$ stretching vibration. The PU cationomer shows a strong peak at 1680 $cm^{-1}$ corre-

**Table II   Tensile Properties, Glass Transition Temperature, and Tan δ Values of PTMG$_{1000}$-based VTPU/MMA Weight Ratio Variation**

| Composition VTPU/MMA | Max Tensile Strength (MPa) | Elongation (%) | Tan $\delta_{max1}$ | $T_{g1}$ (°C) | Tan $\delta_{max2}$ | $T_{g2}$ (°C) |
|---|---|---|---|---|---|---|
| 8/2 | 3.4 | 514 | 0.18 | −45 | 0.19 | 38 |
| 6/4 | 4.7 | 489 | 0.25 | −39 | — | — |
| 5/5 | 4.9 | 429 | 0.63 | −11 | — | — |
| 4/6 | 5.1 | 388 | 0.32 | −32 | — | — |
| 2/8 | 11.6 | 125 | 0.25 | −37 | 0.32 | 31 |

sponding to heterocyclic $>C\!\!=\!\!N$. The shift of the peak to the low-frequency region is due to the electromeric effect arising from quartenization.[14] The FTIR spectrum of PTMG$_{1000}$-based ABCP of 5/5 composition is given in Figure 1. The absence of absorption at 1680 cm$^{-1}$ suggests that the crosslinking is complete.

### Thermogravimetric Analysis

The thermal stability of the crosslinked polymer was evaluated by thermogravimetric analysis (TGA). The TGA curves for the polymers of all compositions based on PTMG$_{1000}$ and those at 5/5 composition of different polyols are given in Figure 2(a,b), respectively. The initial decomposition temperatures were taken as the point of onset. Both composition-variation and polyol-variation specimens show no weight loss up to 260°C, which indicates improved thermal stability.

### Stress–Strain Properties

#### PTMG$_{1000}$-based ABCPs: Effect of Weight Ratio Variation

The stress–strain curves of the samples prepared with the same polyol (PTMG$_{1000}$) and with varying VTPU/MMA weight ratios are shown in Figure 3(a). It can be seen from the Table II that when the MMA content increases the tensile strength increases, while the elongation at break decreases. The inclusion of a large number of polyol chains among MMA molecules leads to the separation of the stiff segments of MMA by a large number of flexible PU segments, thus changing the system. One can also see that the amount of PTMG introduced affects the physical crosslinking. When the VTPU/MMA weight ratio is high (8/2), too many PTMG molecules keep the MMA chains separated from each other and the stress–strain curves exhibit only a smeared yield point. When the PTMG/MMA weight ratio is lower (2/8), there is strong physical crosslinking and, hence, a very sharp yield point. This implies that, depending upon the weight ratios, the ABCPs can be either tough plastics or elastomers.

#### Effect of Polyol Variation

The mechanical properties of VTPU/MMA at 5/5 compositions are shown in Table III. Of all the three systems discussed, PTMG$_{1000}$-based ABCP shows the highest tensile strength. Since the MMA content is the same in all three systems, variations in the properties can be attributed to the number of crosslinks present in the system as well as to the elastomeric behavior of the crosslink soft segment. The stress–strain behavior of ABCPs of the weight ratio 5/5 is represented in Figure 3(b). PTMG$_{1000}$-based ABCP takes a higher stress when compared to the other two systems, because of reorientation of the crystalline phases during stretching. The aliphatic side-

**Table III   Morphological Characteristics, Tensile Properties, Glass Transition Temperature, and Tan δ Values of VTPU/MMA at 5/5 Composition**

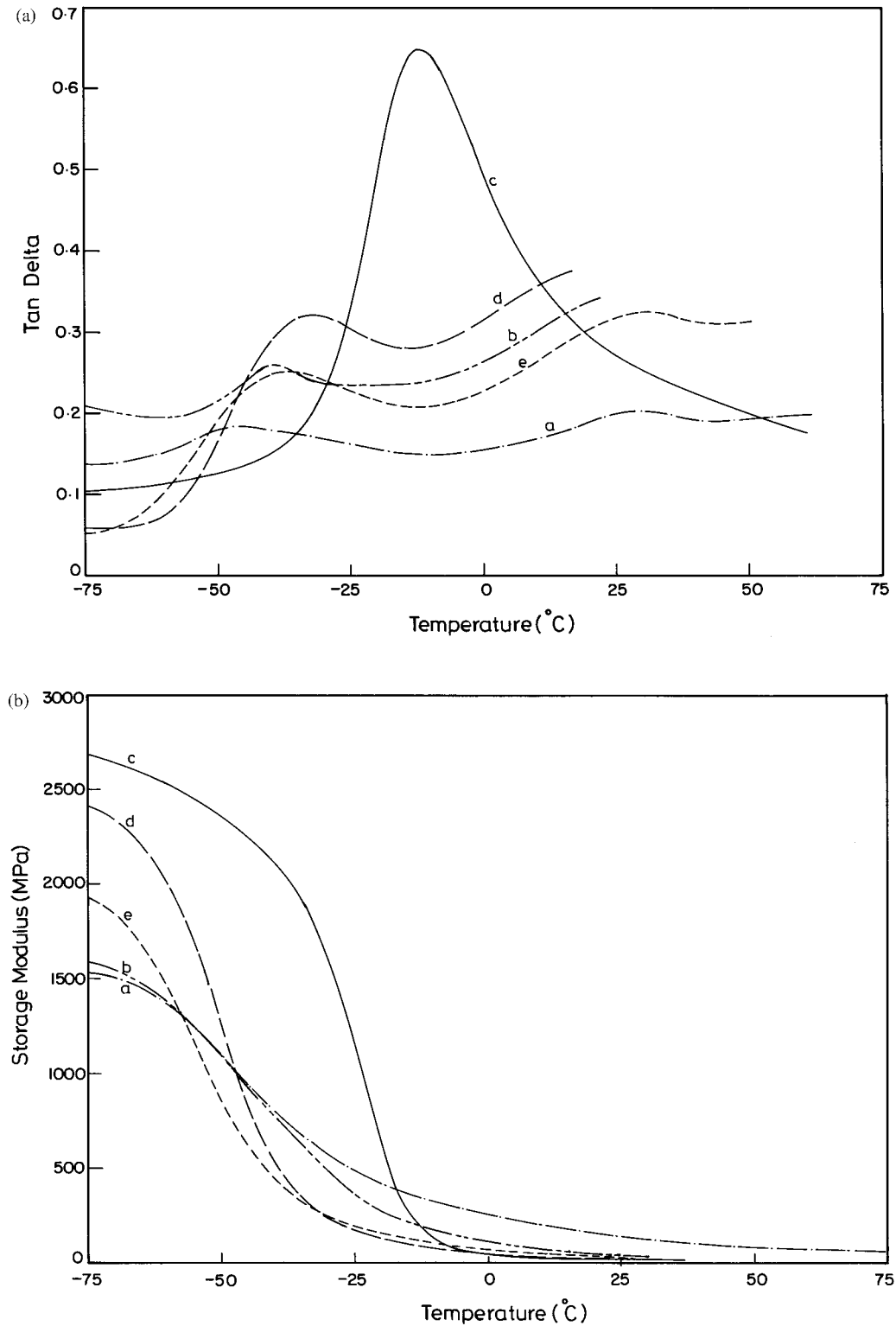| Polyol Variation | Max Tensile Strength (MPa) | Elongation (%) | Tan $\delta_{max1}$ | $T_{g1}$ (°C) | Tan $\delta_{max2}$ | $T_{g2}$ (°C) |
|---|---|---|---|---|---|---|
| PPG$_{1000}$ | 1.61 | 215 | 0.64 | −10 | — | — |
| PTMG$_{1000}$ | 4.90 | 429 | 0.64 | −11 | — | — |
| PCL$_{1250}$ | 2.54 | 475 | 0.31 | −19 | 0.31 | 23 |

**Figure 4**   (a) Tan $\delta$ versus temperature plots of $PTMG_{1000}$-based ABCP [VTPU/MMA weight ratio = (a) 8/2, (b) 6/4, (c) 5/5, (d) 4/6, and (e) 2/8]. (b) $E'$ versus temperature plots of $PTMG_{1000}$-based ABCP [VTPU/MMA weight ratio = (a) 8/2, (b) 6/4, (c) 5/5, (d) 4/6, and (e) 2/8]. (c) Tan $\delta$ versus temperature plots of ABCP [VTPU/MMA weight ratio = 5/5]: (a) $PPG_{1000}$; (b) $PTMG_{1000}$; (c) $PCL_{1250}$.
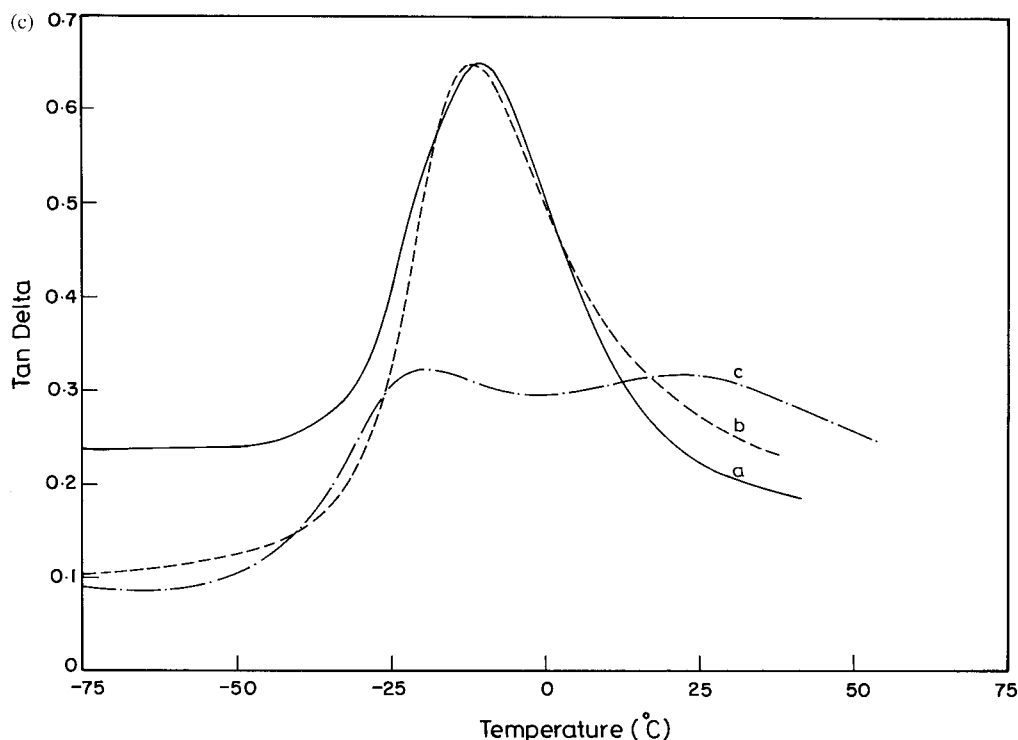
**Figure 4**  (*Continued from the previous page*)

chain groups in $PPG_{1000}$-based ABCPs lower the strength of van der Waal forces between the polymer molecules and, hence, there is a decrease in the tensile strength. Despite the higher crystallinity of $PCL_{1250}$ compared to $PTMG_{1000}$, the tensile strength of the polymer is low. This may be due to the polymer being unoriented, where the crystallites can act as stress concentrators and thereby weaken the material. Higher values of elongation for $PTMG_{1000}$- and $PCL_{1250}$-based ABCPs is due to stress-induced crystallization of soft segments which stops early failure of the samples.

### Dynamic Mechanical Properties

#### *PTMG$_{1000}$-based ABCPs: Effect of Weight Ratio Variation*

The dynamic damping curve against temperature for sample ABCPs with varying weight ratios of VTPU/MMA based on $PTMG_{1000}$ is shown in Figure 4(a). One can observe from Table II that VTPU/MMA of 8/2 and 2/8 compositions present two maxima. There exists a plate area between the two $T_g$'s, which means that the system exhibits a two-phase structure. The upper transition $(T_{g2})$ corresponds to the $T_g$ of the plastic phase,

while the lower one $(T_{g1})$ corresponds to that of the elastomeric phase. On the other hand, VTPU/MMA of 6/4, 5/5, and 4/6 compositions exhibit a single maxima at the intermediate temperature between the $T_g$ of the individual components, indicating there is an extensive interlocking and entanglement between the PU and PMMA matrices. A forced compatibility develops due to the chemical crosslinking and interlocking of the entangled chain that confines phase separation. It is also apparent that at 5/5 composition the peak intensity of tan δ corresponding to $T_{g1}$ is maximum (0.64), covering a broad temperature range, indicating good damping. Figure 4(b) shows the plot of dynamic storage modules $(E')$ versus the temperature for $PTMG_{1000}$-based ABCPs with varying compositions of VTPU/MMA. It is clear that the storage modulus is high for the 5/5 composition in the temperature range −75 to −20°C, depicting relatively higher rigidity.

#### *Effect of Polyol Variation*

The dynamic mechanical relaxation spectra for the samples with a VTPU/MMA weight ratio of 5/5 prepared with three different polyols, namely, $PTMG_{1000}$, $PPG_{1000}$, and $PCL_{1250}$, are shown in Figure 4(c). From Table III, it can be seen that

PPG$_{1000}$- and PTMG$_{1000}$-based ABCPs exhibit a single maxima at the intermediate temperature between the $T_g$ of the individual components, whereas the PCl$_{1250}$-based ABCP exhibits two damping peaks. The double $T_g$ of PCL$_{1250}$-based ABCP is due to the crystalline nature of polycaprolactone diol. The tan δ peak at a higher temperature arises due to the melting of crystallites in the soft segment (PCL) and the tan δ peak at lower temperature arises due to the glass transition temperature of the PU soft segment (elastomeric phase).

## CONCLUSIONS

VTPU/MMA-based ABCPs with (i) varying compositions and (ii) polyol variation at a fixed composition (5/5) were synthesized. Studies with the sample ABCPs showed that the tensile property and the damping behavior were tremendously influenced by the weight variation. PTMG$_{1000}$-based ABCP at a 5/5 composition exhibited higher damping over a broader temperature range.

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