

Thermal degradation of urethanes based on 4,4'-diphenylmethane diisocyanate and 1,4-butanediol (MDI/BDO)

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Differential scanning calorimetry (d.s.c.) and gel permeation chromatography (g.p.c.) were used to study the thermal degradation of 4,4'-diphenylmethane/1,4-butanediol based monodisperse urethane model compounds. It was found that the urethane bond was unstable above 170°C in the crystalline state as well as in the molten liquid state. Significant degradation occurred above 200°C. The annealing time was found to be as important as the annealing temperature. The degradation species present were identified by g.p.c. using an absolute molecular weight-retention volume calibration curve. Polymerization as well as depolymerization occurred during the degradation process, so that the molecular weight distribution tended to broaden. The degradation mechanism was found to be thermal dissociation of the urethanes into free isocyanates and alcohols as confirmed by infra-red spectroscopy and gas liquid chromatography. The degradation rate fits well with first order kinetics with respect to the urethane. The triblocks and oligomeric multiblocks of MDI/BDO/poly(propylene oxide) polyol/polyurethanes were also found to be unstable at elevated temperature.

(Keywords: urethane block copolymers; 4,4'-diphenylmethane diisocyanate/1,4-butane diol; gel permeation chromatography; thermal degradation; differential scanning calorimetry)

INTRODUCTION

Thermoplastic polyurethanes can be formed by reacting diisocyanates, polyols and short chain diols to produce essentially linear polymer chains. The resulting urethane linkages are covalent in nature and reasonably strong, although their stability varies with chemical structure and environmental conditions¹⁻¹¹. At high enough temperature the addition reactions of isocyanate with compounds that have active hydrogens are reversible. The heat lability of the urethane groups is dependent upon the substituents on these groups. Bayer¹ reported the upper stability temperature for the different urethane groups shown in Table 1. Many commercial applications have taken advantage of this reversible thermal dissociation property. The so-called 'blocked' isocyanates or 'splitters', which are widely used in many coating systems, are stable at room temperature, but regenerate free isocyanates at elevated temperature^{12,13}. However, this thermal instability may impose limitations to some applications of thermoplastic polyurethanes. In the presence of high shear stresses and high processing temperature, the urethane linkages may be broken. Some 'scrambling' of polymer segmented structures may occur during polymer melt processing and affect the properties¹⁴. Any thermal treatment of the urethane samples such as annealing at high temperatures and characterization of thermal transitions of high melting urethane compounds need to be carefully interpreted.

This paper deals with the thermal stability of the urethane compounds produced from 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as well as the triblock and multiblock polymers from MDI, BDO and poly(propylene oxide) polyol (PPO).

Camberlin *et al.*¹⁵ indicate that the limited thermal stability of these urethane compounds complicates any study of their thermal transition. The MDI/BDO hard segments with melting point above 180°C were degraded after melting and recrystallization. Hwang *et al.*¹⁶ reported that degradation became detectable by i.r. analysis on samples held above 180°C for more than 5 min. Eisenbach *et al.*¹⁷ also mentioned that the chemical stability of the urethane linkage is limited and a transurethanization reaction occurs at elevated temperature. However, degradation mechanisms and kinetic studies of MDI/BDO urethanes have not been found in the literature.

In the present study, monodisperse model compounds based on MDI and BDO were synthesized¹⁸. Differential scanning calorimetry (d.s.c.) and gel permeation chromatography (g.p.c.) were used to study the thermal degradation of these MDI/BDO based urethane compounds. Degradation kinetics can be readily obtained from the g.p.c. peak heights. The degradation mechanisms were studied by infra-red spectroscopy and gas liquid chromatography (g.l.c.). It was found that both the MDI/BDO pure hard segment oligomers and urethane polymers degrade at elevated temperatures.

Table 1 Thermal stability temperature of different type of urethanes¹

Type of urethane group	Approximate upper stability temperature
Alkyl-NH-CO-O-alkyl	250°C
Aryl-NH-CO-O-alkyl	200°C
Alkyl-NH-CO-O-aryl	180°C
Aryl-NH-CO-O-aryl	120°C

EXPERIMENTAL

Materials

The monodisperse BDO(MDI/BDO)_n urethane model compounds with n = 1,3 were prepared according to the synthetic method of Qin *et al.*¹⁸. To make these model compounds more relevant to the polymers, the hydroxyl end groups were removed by capping with phenyl isocyanate. A triblock with polypropylene oxide polyol in the centre and model hard segments at both ends was also synthesized¹⁸. A random multiblock polyurethane with 48% hard segment content from one step solution polymerization in dimethylacetamide was also included for analysis. The chemical structures of these compounds are given in Table 2.

Differential scanning calorimetry

5–10 mg of the sample was placed in a pierced aluminium pan under dry nitrogen gas atmosphere. The relative heat capacity–temperature curve was obtained at a scan rate of 10°C min⁻¹ on a Mettler TA 3000 system. Temperature calibration was done with a multiple melting point indium–lead–nickel standard. An indium standard was used for enthalpy calibration. Isothermal annealing of the sample at various temperatures for different times was also performed in addition to the regular dynamic scanning.

Gel permeation chromatography

A Waters 150-C ALC/GPC liquid chromatograph with a refractive index detector was used to check the purity of the model compounds and the molecular weight distribution of the degraded samples. Two Du Pont Zorbax PSM 60-S silanized glass bead columns capable of low molecular weight resolution were used. Samples were prepared in N,N'-dimethylformamide (DMF) at 0.1% (w/v) and filtered through 0.45 µm nylon filters. The mobile phase was DMF at a rate of 0.5 ml min⁻¹ and column temperature was maintained at 85°C. The absolute molecular weight calibration was done with the monodisperse urethane compounds as standards.

Infra-red spectroscopy

Spectra were obtained using a Nicolet 60-SX Fourier transform spectrophotometer. A thin film was cast from DMF solution on to a NaCl crystal and the solvent allowed to evaporate. The NaCl salt plate was placed in a heated cell where the temperature was measured with a thermocouple mounted on the cell. Temperature was increased from ambient temperature to approximately 260°C at 10°C intervals and held at each temperature for 5 min. Thirty-two scans were co-added to produce spectra at a resolution of 4 cm⁻¹.

Gas-liquid chromatography

G.l.c. analysis was made on a Hewlett-Packard 5880A gas liquid chromatograph equipped with a flame ionization detector. Separation was accomplished on a 10 × 0.31 mm (i.d.) DB-1 fused silica bonded phase capillary column (J and W Scientific Co.). Hydrogen was used as the carrier gas with a linear velocity of 35 cm s⁻¹. The injection port and detector temperatures were 225°C and 250°C respectively. The column temperature was 70°C and 0.03 µl ethanol extraction of degraded samples was injected with a split ratio of 1 to 60.

RESULTS AND DISCUSSION

Degradation mechanisms

Saunders and Frisch¹¹ summarize the four possible types of reactions that may take place in the thermal decomposition of urethanes. These are shown in Table 3. The propensity for a particular mechanism depends on the chemical nature of the groups adjacent to the urethane linkage and the environmental conditions. Gaylord and Sroog¹⁹ have shown that the reaction of an alcohol with an unsubstituted urethane proceeds the ester interchange or displacement mechanism (i.e. type 4 in Table 3), whereas the same reaction with N-monosubstituted urethanes proceeds through a primary dissociation to the free isocyanate. Griffin and Willwerth⁸ and Marchenko *et al.*² have verified the presence of free isocyanate by infra-red

Table 2 Chemical structures of materials used in this study

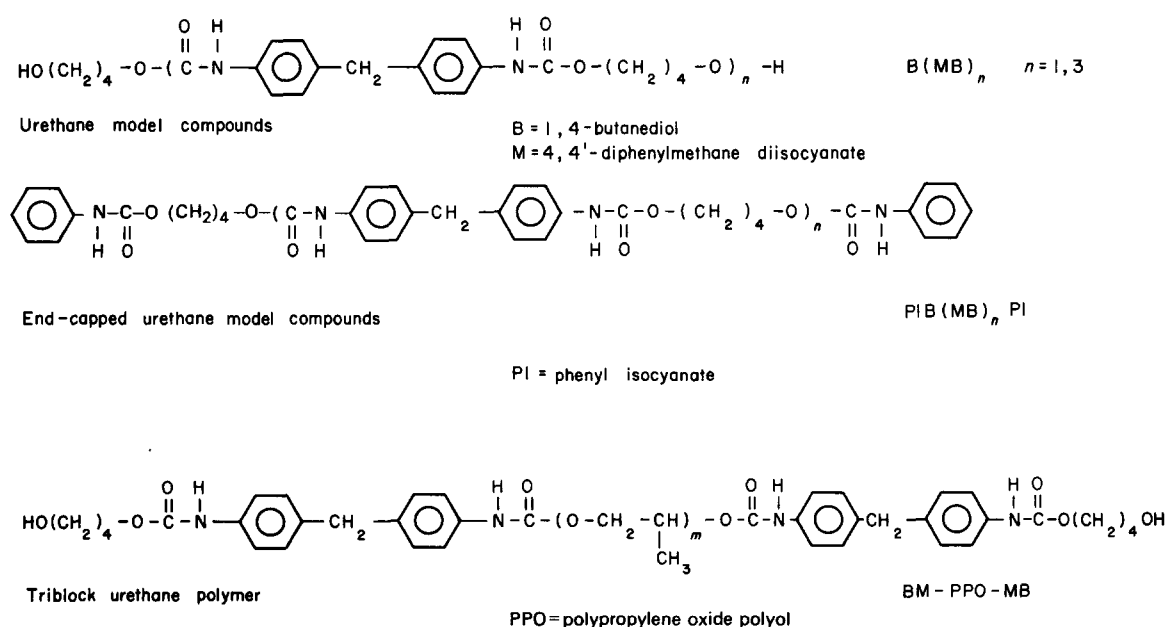
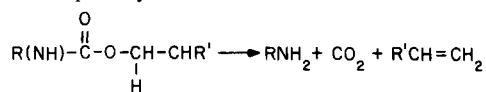


Table 3 Degradation mechanism of urethane upon heating

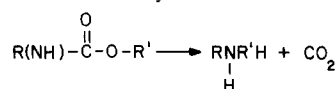
(1) Dissociation to isocyanate and alcohol



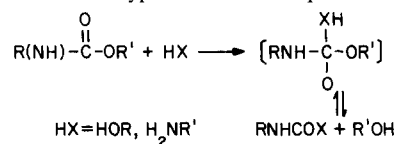
(2) Formation of primary amine and olefin



(3) Formation of secondary amine



(4) Transesterification type bimolecular displacement



when urethanes are heated above 200°C. This supports the first mechanism in *Table 3*.

Since the MDI/BDO based urethanes of interest in this study are *N*-substituted, they would be expected to react through an initial dissociation step. *Figure 1* shows the infra-red spectra of BMB (B=1,4-butanediol, M=4,4'-diphenylmethane diisocyanate, see *Table 2*) at temperatures ranging from 150°C to 260°C. Trace of free isocyanate identified by the 2270 cm⁻¹ absorption band becomes detectable as temperature increases. The same phenomenon was also observed by Harthcock²⁰ in solution polymerized high molecular weight polyurethane. An appreciable amount of free isocyanate was detected above 200°C. Since the -OH end groups of the residual undegraded BMB compounds complicated the identification of the free 1,4-butanediol from the infra-red spectra, g.l.c. was used to identify the presence of 1,4-butanediol. The BMB compound was in a closed glass vial and heated at high temperature. A clear liquid condensed on the wall. Extracted with ethanol, it was identified as free 1,4-butanediol by g.l.c.

Thus, the urethanes thermally dissociate to free isocyanates and alcohols at elevated temperature. This degradation mechanism is further supported by the data of direct pyrolysis in the mass spectrometer, which is an excellent method for monitoring the initial thermal fragmentation processes occurring when polymers are heated to decomposition. Montando²¹ reported the mass spectrum of direct pyrolysis of MDI/BDO based polyurethanes appeared to be essentially that of a mixture of MDI and 1,4-butanediol. Schollenberger¹⁴ also indicated that a significant amount of isocyanate remained in the reaction mixtures owing to the reverse dissociation of urethane linkages when high polymerization temperature was applied. Hence, the degradation mechanism of MDI/BDO urethanes seems to be the type 1 in *Table 3*, i.e. thermal dissociation to isocyanate and alcohol.

D.s.c. and g.p.c. analysis

Thermal analysis has been widely used in urethane literature to characterize the thermal transitions of

polymers. Since the melting endotherms of MDI/BDO hard segments are typically above 200°C, thermal degradation may readily occur during the characterization of the thermal transitions of these compounds. *Figure 2* shows the d.s.c. and corresponding g.p.c. results of B(MB)₃ monodisperse compound (some impurity of B(MB)₅). It is clear in *Figure 2(c)* that the monodisperse B(MB)₃ compound degrades significantly after a typical d.s.c. scan. Polymerization as well as depolymerization occurred during the degradation process, so that the molecular weight distribution tended to broaden. *Figure 3* shows that these new compounds all fall on the same g.p.c. calibration curve as the synthesized narrow hard segments. This also provides support for the degradation mechanism mentioned before. Since all compounds present are B(MB)_n, where *n*=1-10, no other degradation mechanism occurs appreciably. It is interesting to notice in *Figure 2(b)* that even heating at 170°C, ~30°C below the melting point of B(MB)₃, for 2 h causes both chain cleavage and subsequent combination in the solid state. Similar results were obtained when the -OH end groups were removed by capping with phenyl isocyanate.

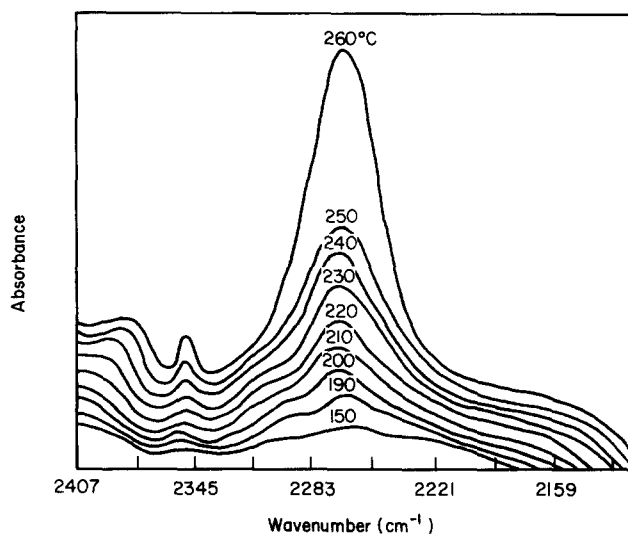


Figure 1 Infra-red spectra of BMB at elevated temperatures. Main peak at 2270 cm⁻¹

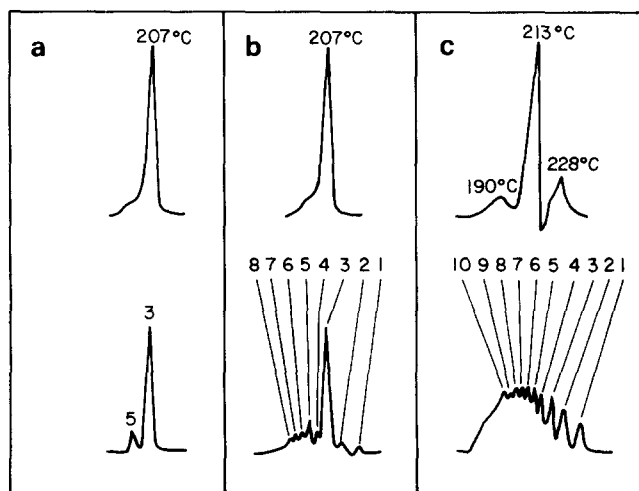


Figure 2 D.s.c. (upper) and g.p.c. (lower) results of B(MB)₃: (a) as precipitated sample from methanol-water solution; (b) annealed at 170°C for 2 h; (c) after 50°C to 250°C d.s.c. scan at 10°C min⁻¹ followed immediately by cooling

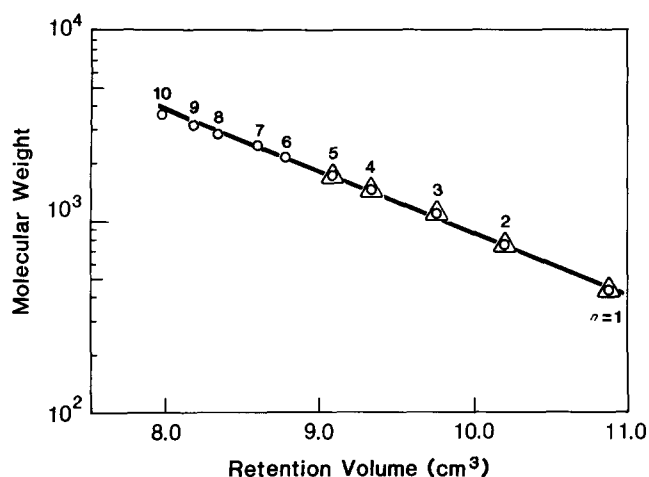


Figure 3 G.p.c. calibration curve for $B(MB)_n$ ($n=1$ to 10); \circ , degraded products; \triangle , synthesized compounds

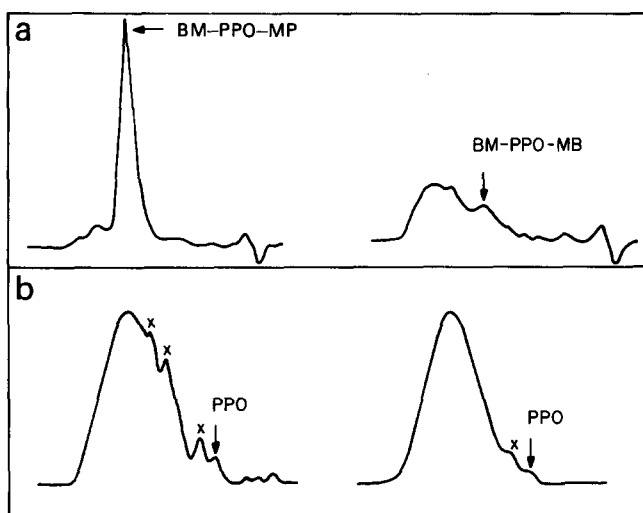
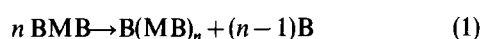


Figure 4 G.p.c. results of (a) degraded triblock and (b) multiblock urethanes. Left, original; right, degraded by d.s.c. heating, 50–250°C at 10°C min⁻¹. (Symbol \times represents the oligomeric multiblock polymers)

However, the singly capped compounds are more susceptible to heating than those capped at both ends. Thus there seems to be a catalytic effect of the OH end group. The triblock BM-PPO-MB and multiblock MDI/BDO/PPO polyurethanes also show the same thermal instability (Figure 4). The distinct oligomeric multiblocks at low molecular weight disappear after a d.s.c. scan from 50°C to 250°C.

Isothermal annealing and degradation kinetics

A series of isothermal annealing experiments at various temperatures for 5 min was carried out on BMB compounds. Parts of the corresponding g.p.c. results are shown in Figure 5. Since peak height represents weight concentration, quantitative analysis of the g.p.c. data is possible. The weight percentages of $B(MB)_n$, $n=0, 1, 2, 3$, are shown in Table 4. Since the g.p.c. peak of 1,4-butanediol was obscured by the DMF solvent, identification from the chromatogram was not possible. Instead, its amount was estimated by assuming that $n-1$ mole of B (1,4-butanediol) were produced accompanying each mole of $B(MB)_n$ generated. This assumption stems from mass balance considerations:



Actually, after the compensation for the free 1,4-butanediol ($n=0$ in Table 4), the calculated MDI to BDO ratios at each temperature agree remarkably well with the theoretical value 0.5. As mentioned above, free 1,4-butanediol was identified by the g.l.c. analysis in the degraded samples, so that qualitative experimental support was provided for the above consideration.

If the degradation kinetics are assumed to be first order with respect to urethanes, the rate expression can be written as

$$\ln \frac{[BMB]}{[BMB]_0} = -kt \quad (2)$$

$$k = k_0 \exp(-E_a/RT) \quad (3)$$

where $[BMB]/[BMB]_0$ is the ratio of residual concentration of BMB compound to its initial concentration, k is the first order constant, A_0 is the pre-exponential factor, and E_a is the apparent activation energy of the reaction. From equations (2) and (3), one obtains

$$2.303 \log_{10} \left[-\ln \frac{[BMB]}{[BMB]_0} / t \right] = \ln k_0 - (E_a/R) \frac{1}{T} \quad (4)$$

Based on the data in Table 4, one may make the Arrhenius plot as shown in Figure 6. The activation energy of degradation obtained from the slope is 25 kcal mol⁻¹ and the pre-exponential factor k_0 is 1.18×10^{12} s. Semenov²² provides a rough estimation for activation energy (kcal) of an endothermic reaction.

$$E_a = 11.5 + 0.75 \Delta H_{rxn} \quad (5)$$

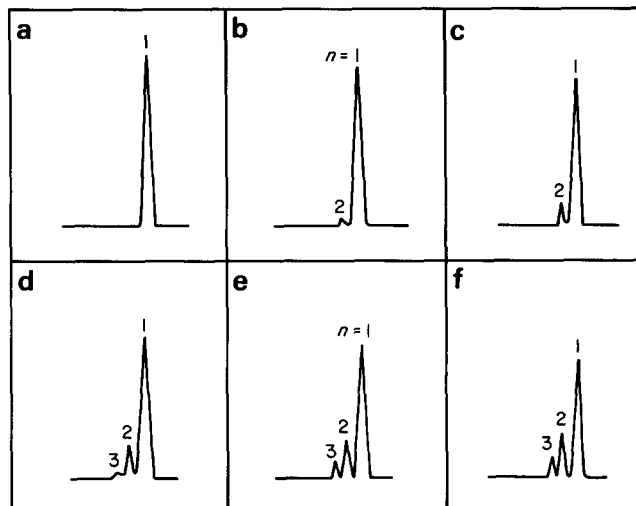


Figure 5 G.p.c. results of BMB after isothermal annealing for 5 min at different temperatures: (a) unannealed BMB; (b) 170°C; (c) 180°C; (d) 190°C; (e) 200°C; (f) 210°C. Peaks labelled with n of $B(MB)_n$

Table 4 Calculated weight percentage of $B(MB)_n$ ($n=0, 1, 2, 3$) based on g.p.c. peak height

Annealing temperature (°C)	n			
	1	2	3	0
170	97.70	2.06	—	0.24
180	94.71	4.72	—	0.57
190	90.62	8.40	—	0.98
200	85.18	11.50	1.70	1.62
210	76.42	17.82	3.17	2.59

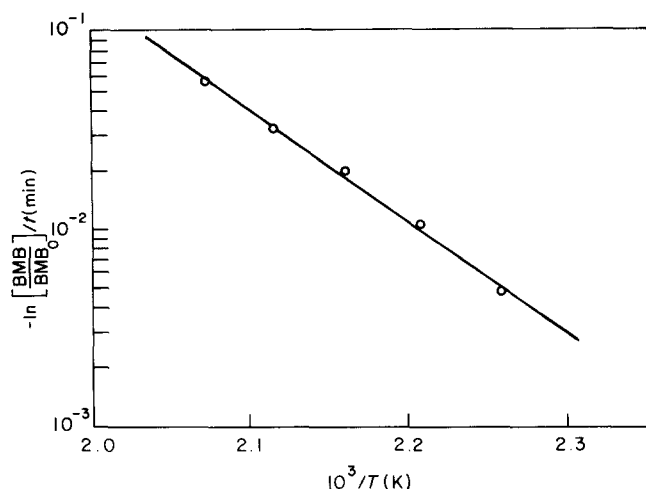


Figure 6 Least square fitting to first order kinetics of urethane BMB degradation based on g.p.c. peak heights. $E_a = 25 \text{ kcal mol}^{-1}$; $k_0 = 1.18 \times 10^{12} \text{ s}$

Substituting $20.3 \text{ kcal mol}^{-1}$ (85 kJ mol^{-1})²³ for ΔH_{rxn} we have $E_a = 26.7 \text{ kcal mol}^{-1}$, which is in reasonable agreement with our result from first order kinetics.

The samples were also annealed at a given temperature for different times. Long annealing time at a lower temperature can cause the same extent of degradation as short annealing time at a higher temperature. Table 4 shows that significant degradation (> 20%) occurs above 200°C, although some degradation has occurred for heating at 170°C for only 5 min. Hence, the dissociation temperature of MDI/BDO based urethanes may be taken as $\sim 200^\circ\text{C}$ from this study, which is in agreement with that reported by Bayer¹ for the aryl-MHCOO-alkyl system in Table 1.

SUMMARY AND CONCLUSION

● Urethanes synthesized from 4,4'-diphenylmethane diisocyanate and 1,4-butanediol dissociate thermally to free isocyanate and alcohol at elevated temperature. Polymerization as well as depolymerization occurs owing to the recombination of the dissociated segments, so that an original monodisperse sample is converted to one with a broad molecular weight distribution.

● When the -OH end groups were capped with phenyl isocyanate, the compounds still degraded in the same fashion although the relative thermal stability was improved. This suggests a catalytic effect of the -OH group to degradation.

● Degradation is possible even in the solid state if annealing time is long enough, i.e. 2 h at 170°C. Annealing time is as important as the applied temperature in degradation.

● The temperature at which significant degradation of these MDI/BDO urethanes occurs may be taken as $\sim 200^\circ\text{C}$.

● Triblock BM-PPO-MB and multiblock polymers from MDI/BDO/PPO show similar degradation as the pure MDI/BDO hard segments.

One might ask what is the significance of this kind of thermal degradation and how it may affect the properties and processing of the polyurethanes. Some conclusions are summarized as follows:

● In any experiment involving thermal treatment of

polyurethanes, such as melt rheology studies, annealing for phase separation study and characterization of thermal transitions etc., the possibility of degradation must be born in mind and data should be carefully interpreted.

● If the degradation is a complete random scission process, one may expect a most probable molecular weight distribution. However, if some impurity such as moisture is present in systems, it may react with the isocyanate-terminated cleaved polymer chains, so that the average molecular weight is reduced and the molecular weight distribution broadened.

● The isocyanate-terminated cleaved ends may attack the urethane sites and cause chemical crosslinking through allophanate reaction under certain conditions. Some d.s.c. samples after prolonged heating became insoluble in DMF.

● Degradation must predominate in the areas of highest urethane group concentration, i.e. the hard segment domains. The broadening of the hard segment sequence length distribution may affect the crystallinity of the hard segment domains and cause high temperature dependence of the storage modulus due to the lower extent of phase separation.

● In thermoplastic processing under high temperature and shear stresses and in reaction injection moulding during which the temperature in the centre of the mould may exceed 200°C owing to the high reaction exotherm, thermal degradation may occur. This thermal dissociation may not be totally disadvantageous from the processing point of view since it allows molecular rearrangements by breaking the already made urethane bonds. This may be of particular interest in the processing of RIM systems that have undergone premature phase separation. By breaking the urethane bonds in those precipitated hard segment domains, the soft segments may then be incorporated to increase the molecular weight and form a highly interconnected morphology. In a separate paper, the thermal dissociation of urethanes has been shown to influence the crystalline structure and morphology by breaking up the original network²⁴.

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REFERENCES

- 1 Bayer, O. 'Das Diisocyanate-Polyadditions Verfahren', Carl Hanser Verlag, Muenchen, 1963
- 2 Marchenko, G. N., Fedoseev, M. S. and Rogov, N. G. Ch. 13 in 'Soviet Urethane Technology', Technomic, Conn., 1973
- 3 Mukaiyama, T., Motoki, S. and Hamada, Y. *J. Am. Chem. Soc.* 1953, **26**, 49
- 4 Mukaiyama, T. and Hoshino, Y. *J. Am. Chem. Soc.* 1956, **78**, 1946
- 5 Mukaiyama, T. and Iwanami, M. *J. Am. Chem. Soc.* 1957, **79**, 73
- 6 Mukaiyama, T., Motoki, S. and Hamada, Y. *Bull. Chem. Soc. Jpn.* 1953, **26**, 49
- 7 Mukaiyama, T., Akiba, T. and Asahi, T. *Bull. Chem. Soc. Jpn.* 1960, **33**, 1137

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- 8 Griffin, G. Willwerth, L. *I & EC Prod. Res Devel.* 1962, **1**, 265
- 9 Fabris, H. J. *Adv. Urethane Sci. Technol.* 1978, **4**, 89
- 10 Dorofeeva, I. B. and Tarakanov, O. G. *Zh. strukt. khim.* 1984, **25**(4), 129
- 11 Saunders, J. H. and Frisch, K. C. 'Polyurethanes Chemistry and Technology', Part I, pp. 106–121, Wiley–Interscience, New York, 1962
- 12 Saunders, J. H. and Frisch, K. C., *ibid.*, Part II, Ch. VIII, Wiley–Interscience, New York, 1962
- 13 Dombrow, B. A. 'Polyurethanes', p. 31, Reinhold, New York, 1965
- 14 Schollenberger, C. S., Dinbergs, K. and Stewart, F. D. *Rubber Chem. Tech.* 1982, **55**, 137
- 15 Camberlin, Y., Pascault, J. P., Letaffe, J. M. and Claudy, P. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 383
- 16 Hwang, K. K. S., Wu, G., Lin, S. B. and Cooper, S. L. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1677
- 17 Eisenback, C. D. and Gunter, Cl., *Polym. Prepr.* 1985, **26**(2), 7
Polyurethane Elastomers, Brighton, Mass., June 1984
- 18 Qin, Z. Y., Macosko, C. W. and Willinghoff, S. T. *ACS Meeting, Polym. Mat. Sci. Eng. Preprints* 1983, **49**, 239; *Macromolecules* 1985, **18**(3), 553
- 19 Gaylord, N. G. and Sroog, C. E. *J. Org. Chem.* 1953, **18**, 1632
- 20 Harthcock, M. A., personal communication, Dow Chemical, Freeport, Texas, February 1985
- 21 Montando, G., Puglisi, C., Scamporrino, E. and Vitalini, D. *Macromolecules* 1984, **17**, 1605
- 22 Semenov, N. N. 'Some problems in Chemical Kinetics and Reactivity', Vol. I, pp. 29 and 64, (translated by M. Boudart), Princeton Univ. Press, Princeton, N.J., 1958
- 23 Pannone, M. C. *MS Thesis*, University of Minnesota, 1985
- 24 Kolodziej, P., Yang, W. P., Macosko, C. W. and Willinghoff, S. T. 'Impingement Mixing and Its Effect on the Microstructure of RIM Polyurethanes', *J. Polym. Sci., Polym. Phys. Edn.* 1986, in press