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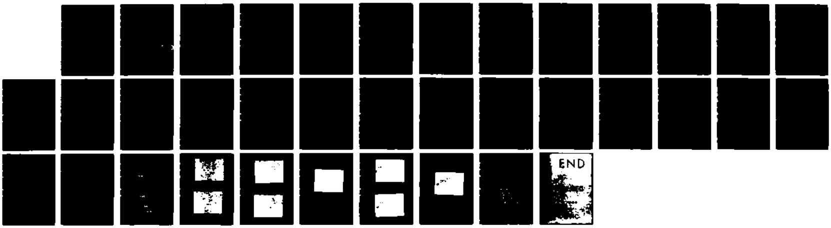

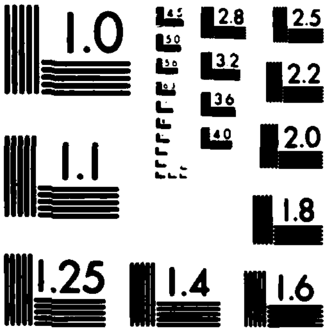

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TECHNICAL REPORT No. 4

# STRUCTURE-PROPERTY RELATIONSHIPS IN THERMOPLASTIC ELASTOMERS:

## I. SEGMENTED POLYETHER-POLYURETHANES

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# Structure-Property Relationships in Thermoplastic Elastomers:

## I. Segmented Polyether-Polyurethanes

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### Synopsis

Segmented poly(ether-*b*-urethanes) have been synthesized with 2000 MW polypropylene oxide coupled with diisocyanates and diol type chain extenders. The diisocyanates used were symmetric rigid 4,4'-diphenylmethane diisocyanate (MDI), linear aliphatic hexamethylene diisocyanate (HDI) and unsymmetric rigid toluene-2,4-diisocyanate (TDI). The chain extenders were symmetric N,N'-bis(2-hydroxyethyl) terephthalamide (BT) and N,N'-bis(2-hydroxyethyl)-hydroquinone (BH) unsymmetric N,N'-bis(2-hydroxyethyl)isophthalamide, and linear aliphatic butanediol (B). Hard segment contents ranged from 20 to 40 wt %. The thermal behavior of these materials is consistent with phase separation into separate hard and soft domains. In order of increasing temperature above the soft segment Tg, there are transitions which occur in the regions -56 to -36°C ($T_a$), 70 to 90°C ($T_b$) and 138 to 168°C ($T_m$). The former is probably associated with soft segment change from a viscoelastic to an elastomeric state; the values of $T_a$ are ~ -51°C and -56°C for the

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MDI-BT and HDI-BT polymers, respectively, which are independent of hard segment content. Microscopy showed the former to have spherulitic morphology, so these materials have good microphase separation and exhibit crosslinked elastomeric properties. The TDI-BT or BI and MDI-B polyurethane have composition-independent $T_a$ values of -41°C and -36°C, respectively. These materials probably have considerable "domain-boundary-mixing". At low hard segment content the MDI-B polymers behave as non-crosslinked elastomers. Only the MDI-BI polymers have $T_a$ values, which are strongly affected by composition, increasing in magnitude with increasing of hard segment content. This is interpreted as significant "mixing-in-domains" and is supported by morphology observed by microscopy. The next higher transition, $T_b$, probably involves dissociation of interdomain hydrogen bonding. In the case of the MDI-BT polyurethanes, the spherulites associated with the hard domains had disappeared at 141°C and the few small spherulites in the MDI-BI polymers disappeared at 130°C. The $T_b$ values are 70°C, 83-90°C and 100°C for the MDI-B, HDI-BT and HDI-BI polymers, respectively. The melting transitions occurred between 138°C to 168°C for the various polyurethanes except for the MDI-BT systems which decompose before melting. Thermal decomposition is a two-stage process. Hard segments decompose between 200 and 300°C. The initial decomposition temperatures are lowered in the presence of strong acid. Soft segments decompose at higher temperatures. The mechanical properties of the MDI-BI polyurethanes showed crosslinked elastomer behaviors at high hard segment content but acts as uncrosslinked material at high soft segment compositions.

## INTRODUCTION

Thermoplastic elastomers are interesting materials because of their useful properties which can be varied by the choice of the structural units. They are block copolymers having either segmented blocks $(AB)_{\underline{n}}$, linear triblocks ABA, or radial multiblocks, $AB_{\underline{n}}$. Our research effort has two main objectives. The first is to determine structure-property relationships for the three types of thermoplastic elastomers prepared from the same A and B building blocks. The second is to incorporate specific physical properties by synthesis of building blocks of appropriate chemical structures.

Polyurethane thermoplastic elastomers are linear segmented block copolymers of the $(AB)_{\underline{n}}$ type. It is usually comprised of blocks of soft segments with low $T_g$ separated by hard segments having either high $T_g$ or is semicrystalline. The latter provides dimensional stability by acting as multifunctional physical crosslinks. The system is characterized by microphase separation, the driving force of which is the incompatibility of the two segment types and in the case of polyurethanes this is enhanced by the formation of interurethane hydrogen bonds. There are ample experimental evidence that the phase separation is incomplete but exhibit some degree of phase mixing.[1-5]

There are several ways to influence the phase separation processes. One method is to decrease the polarity of the soft segment since the urethane groups are highly polar. For instance, the degree of phase separation increases in the order of polyester,[3] polyether,[4,5] polybutadiene,[6] and polyisobutylene[7] as the soft segments.

The central purpose of this work is to study systematically the effect of variation of the structure of the hard segment using different diisocyanates and chain extenders and the amount of polyether soft segments on the mechanical, thermal and rheological properties of the block copolymers and the effect of filler on them.

## EXPERIMENTAL

### Materials

Hydroxy-terminated poly(propylene oxide), PPO, molecular weight 2000, was obtained from Polysciences. The functionality was 2.0 as determined by the Karl Fischer method. 4,4'-Diphenylmethane diisocyanate (MDI) from Mobay Chemicals and hexamethylene diisocyanate (HDI) and 2,4-toluene diisocyanate (TDI), both from Aldrich Chemicals, were vacuum distilled immediately before use. The chain extenders 1,4-butandiol, **B** and bis(2-hydroxyethyl)hydroquinone, **BH**, were obtained from Aldrich Chemical Co. N,N'-bis(2-hydroxyethyl)terephthalamide, **BT**, and N,N'-bis(2-hydroxyethy)-isophthalamide, **BI**, were synthesized by aminolysis of the corresponding phthalate esters using 2-aminoethanol. All chain extenders were purified prior to use.

### Synthesis

The segmented block copolymers were synthesized by a two stage process. PPO was first capped by an appropriate amount of MDI at 60 - 70°C in the presence of dibutyltin dilaurate (0.5% by weight). Then chain extender was added, and chain extension was allowed to proceed at room temperature for 4 hrs in DMF solution. The reaction was terminated by the addition of methanol. Solvent was removed by evaporation, and the product was dried at 60 - 70°C for

48 hrs under high vacuum. These copolymers are designated as PEPU (polyetherpolyurethane) followed by the abbreviated name of the chain extender (see above) and three numbers in parentheses indicating the molar ratios of the three reactants. For instance PEPU-BT(1-3-2) corresponds to the copolymers prepared from one mole of PPO, three moles of MDI and two moles of BT, etc.

### Characterization

Intrinsic viscosities were obtained in DMF solution at 25°. A Waters Associates 201 Chromatograph equipped with five micron styrogel columns was used to determine the molecular weights of the copolymers dissolved in THF except for HDI polyurethanes which were dissolved in N-methylpyrrolidone. The data were analyzed using the universal calibration method versus polystyrene standards.

Thermogravimetric analysis (TGA) curves were obtained with a Perkin-Elmer TGS-II instrument at a heating rate of 20° $min^{-1}$ and a nitrogen atmosphere flowing at 0.8 $cm^3$ $min^{-1}$. Differential scanning calorimetric data were measured with a Perkin-Elmer DSC-II apparatus with a 20° $min^{-1}$ heating rate.

Tensile properties of copolymer films cast from DMF were obtained with an Instron Tester at a strain rate of 1 cm $sec^{-1}$.

## RESULTS AND DISCUSSION

### Structures of Polyurethanes

A number of copolymers were synthesized varying the chain extender and composition of reactants. The structure data of the polyurethanes given in Table I are prepared from the same PPO soft segment and MDI with different chain extenders. The molar ratios were varied to change the amount of hard

## Table I

### Structures and Properties of Segmented Poly(ether-b-urethane) From MDI

| Polymer[a] | DC[b] | wt % HS[c] | $\bar{M}_n \times 10^{-4}$ | $\bar{M}_w / \bar{M}_n$ | $[\eta]$ $dl g^{-1}$ | DSC °C $T_a$ | $T_b$ | $T_m$ |
|---|---|---|---|---|---|---|---|---|
| BT(1-3-2) | 9.5 | 39 | 3.1 | 2.2 | 0.43 | -51 | 133 | ---[d] |
| BT(1-2.5-1.5) | 10 | 33 | 3.1 | 2.1 | 0.39 | -51 | 134 | ---[d] |
| BT(1-2-1) | 11 | 27 | 3.1 | 2.3 | 0.36 | -52 | 133 | ---[d] |
| BT(1-1.67-0.67) | 12 | 23 | 3.0 | 2.2 | 0.35 | -51 | 133 | ---[d] |
| BI(1-3-2) | 9.5 | 39 | 3.1 | 2.0 | 0.24 | -23 | 127.5 | 168.5 |
| BI(1-2.5-1.5) | 10 | 33 | 3.1 | 1.8 | 0.24 | -35 | 127.5 | 168.5 |
| BI(1-2-1) | 16 | 26 | 4.4 | 1.7 | 0.65 | -48 | 132 | 164 |
| BI(1-1.67-0.67) | 12 | 23 | 3.1 | 1.9 | 0.23 | -50 | 127.5 | 161 |
| BI(1-1.5-0.5) | 12 | 20 | 3.1 | 1.8 | 0.22 | -52 | 127.7 | 155 |
| BH(1-2-1) | 12 | 26 | 3.2 | 1.9 | 0.37 | ---[e] | 99.5 | ---[d] |
| B(1-2-1)[f] | 5 | 23 | 1.3 | 1.7 | 0.12 | -36 | 70 | 140 |
| B(1-2-1)[g] | 8 | 23 | 2.1 | 2.4 | 0.29 | -36 | 70 | 138 |
| B(1-2-1) | 22 | 23 | 5.6 | 1.5 | 0.52 | -36 | 70 | 138 |
| B(1-3-2)[g] | 11 | 32 | 3.3 | 3.8 | 0.34 | -36 | 10 | 138 |

[a] Polymerization catalyzed by dibutyltin dilaurate unless otherwise stated; [b] Degree of condensation (see text); [c] wt % hard segment; [d] Polymer decomposes before melting; [e] Too weak in DSC; [f] No catalyst; [g] Catalyzed by triethylamine.

segments. Table II contains the data for polyurethanes made with TDI and HDI.

In Tables I and II the values of $\bar{M}_n$ should be taken as significant only in the relative sense. The GPC column used was rated for $\bar{M}_n$ of ca. 30,000. For polymer with about this $\bar{M}_n$ GPC gave the most probable distribution of $\bar{M}_w/\bar{M}_n \sim 2.1 \pm 0.1$. However, both lower and higher polydispersity indices were obtained for some of the polymers, especially those with high molecular weights.

The degree of condensation, DC corresponds to the average number of structural unit per chain if the polymerization had proceeded according to theory. Thus, for BI$(1\text{-}2_m\text{-}1)$ the DC value is $\bar{M}_n \cdot \{1 \times 2000$ (MW of PPO) $+ 2 \times 250$ (MW of MDI) $+ 1 \times 252$ (MW of BI)$\}^{-1}$. Similarly, wt % of hard segment (HS) is based on complete polymerization according to stoichiometry. The value of DC is about twice as large for butanediol as for the aromatic chain extenders owing partly to their poor solubilities and lower reactivities.

The polymerization is slow uncatalyzed. Of the two catalysts compared, dibutyltin dilaurate is superior to triethylamine. Table I showed that MDI-B(1-2-1) polyurethanes formed without and with amine and tin catalysts have $\bar{M}_n$ values in the ratio of 1:2:5. Consequently, all the other polymerizations were carried out with the tin catalyst.

## Molecular Weight-Viscosity-Structure Relationship

Tables I and II contain interesting data of molecular weight, wt % HS and viscosity. For the same molecular weight, $[\eta]$ decreases with decreasing wt % HS for the copolymers obtained with MDI and BI. With comparable hard segment content $[\eta]$ increases with increasing MW for the MDI and B systems.

## Table II

### Structures and Properties of Segmented Poly(ether-*b*-urethane) From TDI and HDI

| Polymer[a] | wt % HS[c] | $\overline{M}_n \times 10^{-4}$ | $\overline{M}_w \times 10^{-4}$ | $\frac{\overline{M}_w}{\overline{M}_n}$ | [η] dl g$^{-1}$ | DSC °C | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $T_a$ | $T_b$ | $T_m$ |
| Isocyanate | | | | | | | | |
| TDI | | | | | | | | |
| BT(1-3-2) | 34 | 3.2 | | 2.0 | 0.18 | -43 | 62 | 153 |
| BT(1-2.5-1.5) | 29 | 4.5 | | 2.2 | 0.20 | -39 | 60 | 160 |
| BT(1-2-1) | 23 | 6.3 | | 2.1 | 0.26 | -39 | 60 | 157 |
| BI(1-3-2) | 34 | 3.1 | | 1.9 | 0.15 | -42 | 58 | 159 |
| BI(1-2.5-1.5) | 29 | 4.1 | | 2.1 | 0.17 | -42 | 58 | 154 |
| BI(1-2-1) | 23 | 4.1 | | 2.1 | 0.17 | -42 | 58 | 166 |
| HDI | | | | | | | | |
| BT(1-3-2) | 34 | n.d.[c] | 5.6 | | n.d. | -58 | 98 | ---[d] |
| BT(1-2.5-1.5) | 29 | n.d. | 5.6 | | n.d. | -57 | 100 | ---[d] |
| BT(1-2-1) | 23 | n.d. | 5.5 | | 0.39 | -57 | 102 | 146 |
| BI(1-3-2) | 34 | n.d. | 5.2 | | 0.21 | -57 | 90 | 147 |
| BI(1-2.5-1.5) | 29 | n.d. | 5.2 | | 0.17 | -55 | 86 | 144 |
| BI(1-2-1) | 23 | n.d. | 7.2 | | 0.32 | -55 | 83 | 143 |

[a] All polymerizations catalyzed by dibutyltin dilaurate; [b] wt % hard segment; [c] Not determined; [d] Too weak in DSC.

These relationships are characteristic for the para aromatic MDI, BT, and BH and short linear B constituents, suggestive of more extended chain configuration for the hard segment, i.e. rigid rod-like. When the chain extender is the meta substituted BI, then the polyurethanes made with MDI has [η] independent of either % HS or MW. This is, of course, also true for the system containing both meta compounds BI and TDI. The solution properties of copolymers made from TDI and BT, there are only weak relationships between viscosity, % HS and MW. In Table II the small increase in [η] with two-fold increases in $\bar{M}_n$, i.e. BT(1-3-2) and BT(1-2-1), may be due to partial compensation by the decrease in hard segment content.

## Thermal Transitions

The thermal behaviors of various polyether and polyester urethane elastomers, such as heat capacity, linear expansion, and tensile strength have been investigated by Miller and Saunders,[8] and Clough and Schneider.[9] We find the $T_g$ of poly(ether-b-urethanes) with butanediol of compositions 1-3-2 and 1-2-1 is -113°C. The other polyurethanes of this work are expected to have their $T_g$ values in this region because they have the same soft blocks. However, the width of the transition may be influenced by the soft phase homogeneity and its exact temperature may be affected by the extent of microphase separation.

There are three or more transitions at temperatures above $T_g$.[10,11] The lowest temperature one, designated as $T_a$ in Table I and II was proposed by Miller and Saunders[8] to reflect a change from state with viscoelastic to one with elastomeric mechanical behavior. On the other hand, other workers[12,13] referred to the transitions for polyurethanes of PPO-2000 coupled with MDT and N-methyl diethanolamine between -16 and -33°C to be their $T_g$'s. We found $T_g$ to be -113°C for polyurethanes with PPO soft segments.

Tables I and II gave the values of $T_a$; they appear to depend upon the nature of the hard segment. All the HDI polyurethanes chain extended with either BT or BI have the same $T_a$ of -56.5 ± 1.5°C independent of the copolymer compositions. For the MDI polyurethanes chain extended with BT, they have nearly the same composition invariant $T_a$ value of -51 to -52°C. A probable interpretation is that the microphase separations in these systems are complete as will be shown by microscopy of formation of large spherulites. These polyurethanes will be referred to as class A.

The $T_g$'s of the other polyurethanes can be grouped into two other classes. In one class, B, the values of $T_a$ are independent of the copolymer compositions but their magnitudes were much higher than those of class A. All the TDI polyurethanes with either BT or BI chain extenders have -41.5 ± 1.5°C for $T_a$. The $T_a$ value is -36° for the PPO-MDI-B polyurethanes. It is likely that there are mixing of soft and hard segments in the domain boundaries. Greater degree of mixing can raise the temperature for the conversion of the soft phase from a viscoelastic to an elastomeric material. According to this interpretation the "domain-boundary mixing" in the PPO-MDI-B system is greater than the PPO-TDI polyurethanes containing BT and BI.

Finally, in the case of PPO-MDI-BI (class C) the values of $T_a$ increase from -52°C for 20% HS to -23°C for 39% HS. In this system there may be extensive mixing of both types of segments in their respective domains.

The above interpretations are still speculative, more studies with techniques such as SALS, SAXS, neutron scattering, etc. are needed for further clarification.

The transition above $T_a$ is designated $T_b$. The value of $T_b$ seems to be characteristic for a given diisocyanate-chain extender system but relatively insensitive to the copolymer composition. However, we hasten to add that $T_b$ values for each system are less constant than the $T_a$ values for class A and B polyurethanes. For MDI copolymers, $T_b$ values are 133 - 138°C for BT, 127.5 - 132°C for BI, 99.5°C for BH, and 70°C for B chain extenders. In the case of TDI systems, BT extended polyurethanes have $T_b$ of 60 - 62°C and is 58°C for the BI extender. The $T_b$ values for HDI polyurethanes are 98 to 102°C and 83 to 90°C for the BT and BI chain extenders, respectively. In the last group there appears to be consistent variation of $T_b$ with % HS. However, increase of % HS increases $T_b$ with BT but decreases $T_b$ for BI extenders.

Clough and Schneider[9] proposed that $T_b$ is related to the dissociation of hydrogen bonds between the urethane secondary amine and the ether oxygen atoms of PPO. Hot stage microscopic structures suggest that it is the dissociation of interdomain hydrogen bonds which largely determine the magnitude of $T_b$. On the other hand van Bogart et al.[15] suggested that $T_b$ is an interdomain phenomenon of annealing-induced ordering. Our results are not consistent with the former view; there is no correlation between $T_a$'s and $T_b$'s of the various polyurethanes studied here. On the other hand if intradomain ordering processes are involved, one might expect a greater variation of $T_b$ for class C systems with "mixing-in-domains" which was not observed. If one ignores the "mixing-in-domains" effect, then the magnitude of $T_b$ is largely determined by the hard domain structures with $T_b$ decreasing in the order of MDI-BT(BI) > HDI-BT(BI) > TDI-BT(BI) > MDI-B. Probably both types of interactions contribute to varying degrees depending upon the particular polyurethane.

Finally, the highest temperature transition is quite likely to be the melting of the hard segment domains. $T_m$ values range from 140 to 168.5°C except for the MDI-BT system which apparently decomposes before melting. For the most extensively studied MDI-BI polymers, there is a definite decrease of $T_m$ value with decreasing HS segment content (Table I). In the other systems there are either little dependence on $T_m$ values showing no relationship to % HS within a narrow range of % HS

## Thermal and Acid Catalyzed Decomposition

The thermal stability was polyurethanes were investigated with TGA. In majority of the cases the polymer decomposes in two stages; a typical thermogram is shown in Figure 1. The onset of weight loss, $T_o$, occurs between 200 and 220°C for MDI, at 160°C and 182°C for TDI and HDI, respectively with BT and BI chain extenders. The first stage weight loss is complete at *ca* 300°C for all polyurethanes. This is followed by a plateau and then rapid decomposition which has maximum rate in the vicinity of 390°C. In some cases there is a plateau region separating the two stages of decomposition. Instead of presenting a large number of TGA curves, the results are summarized in Table III in the form of $T_o$, $T_{10}$ and $T_{50}$ corresponding to temperatures for onset, 10% weight loss and 50% weight loss, respectively. The polyurethane with MDI and BB has $T_o$ = 237°C and 2-stage TGA curve. The only exceptions are the butandiol extended copolymers which have single stage TGA curve, the $T_o$

## Table III

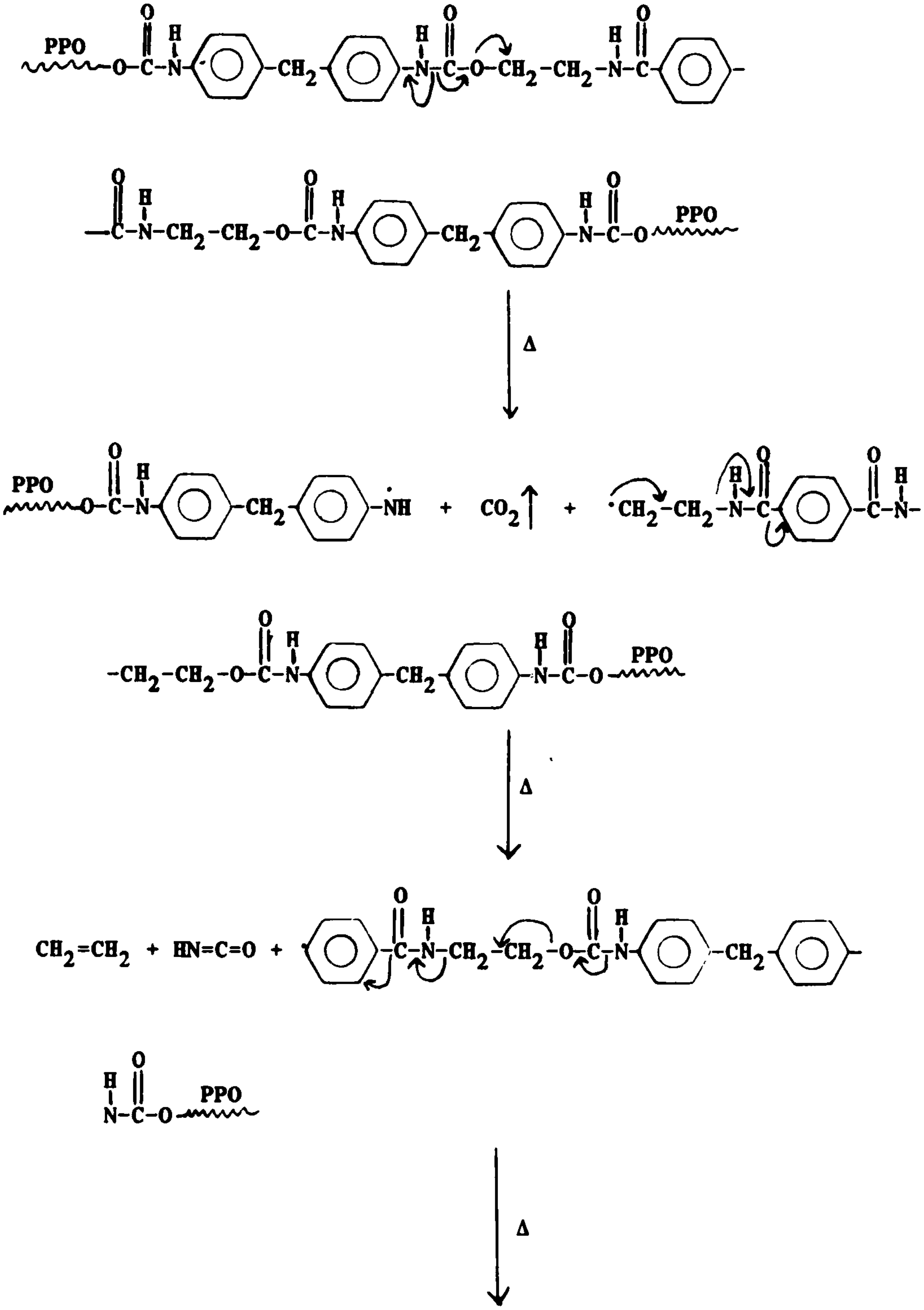
### TGA Results for Poly(ether-b-urethane)

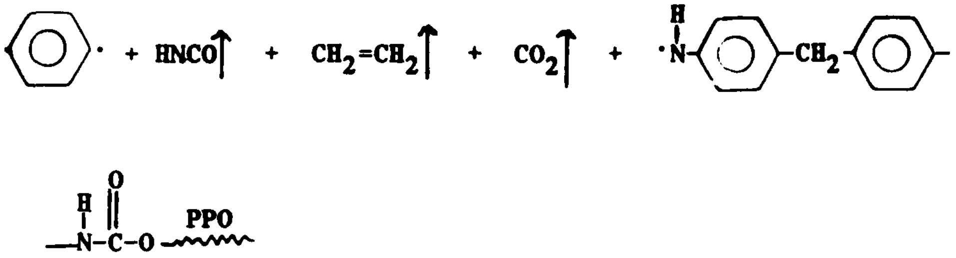
| Polymer | | | Decomposition Temperatures | | | | | |
|---|---|---|---|---|---|---|---|---|
| Diiso-cyanate | Composition | Chain Extender | $T_o$ | $T_o'$[a] | $T_{10}$ | $T_{10}'$ | $T_{50}$ | $T_{50}'$ |
| MDI | 1-3-2 | BT | 200 | 87.5 | 287.5 | 220 | 383 | 385 |
| | 1-2.5-1.5 | | 200 | --[b] | 290 | --- | 345 | --- |
| | 1-2-1 | | 200 | 115 | 290 | 317 | 390 | 390 |
| | 1-1.67-0.67 | | 200 | 135 | 307 | 320 | 376 | 394 |
| MDI | 1-3-2 | BI | 200 | 135 | 290 | 307.5 | 387 | 390 |
| | 1-2.5-1.5 | | 200 | --- | 276 | --- | 371 | --- |
| | 1-2-1 | | 224 | 200 | 290 | 290 | 354 | 386 |
| | 1-1.67-0.67 | | 200 | 135 | 314 | 315 | 386 | 393 |
| MDI | 1-3-2 | B | 250 | 151 | 320 | 270 | 387 | 375 |
| | 1-2-1 | | 275 | 220 | 350 | 340 | 395 | 395 |
| MDI | 1-2-1 | BH | 237 | 182 | 313 | 291 | 365 | 355 |
| TDI | 1-3-2 | BT | 160 | 108 | 260 | 282 | 362 | 382 |
| | 1-2.5-1.5 | | 160 | 108 | 265 | 295 | 372 | 392 |
| | 1-2-1 | | 160 | 108 | 275 | 310 | 378 | 375 |
| TDI | 1-3-2 | BI | 160 | 107 | 265 | 265 | 347 | 327 |
| | 1-2.5-1.5 | | 160 | 107 | 287 | 287 | 355 | 381 |
| | 1-2-1 | | 160 | 107 | 287 | 287 | 372 | 381 |
| MDI | 1-3-2 | BT | 182.5 | --- | 272.5 | --- | 344 | --- |
| | 1-2.5-1.5 | | 182 | --- | 295 | --- | 377 | --- |
| | 1-2-1 | | 182.5 | --- | 300 | --- | 372 | --- |
| HDI | 1-3-2 | BI | 182.5 | --- | 294 | --- | 368 | --- |
| | 1-2.5-1.5 | | 182.5 | --- | 305 | --- | 376 | --- |
| | 1-2-1 | | 182.5 | --- | 292.5 | --- | 360 | --- |

[a] With 1% p-toluene sulfonic acid added; [b] Not determined.

values are much higher than the others.

The two stage TGA curve suggests that one of the domains is decomposing at low temperature than the other. The following observations show that it is the chain extension segment in the hard domain which undergoes decomposition first. Table IV gives the weight loss at 300°C which corresponds to completion of the first stage decomposition. This is compared with the theoretical loss calculated for [wt of chain extender + wt of 2 eqs CO]/[total wt of polymer]. They are in good agreement for all the MDI polyurethanes. The following mechanism may be proposed for the thermal degradation processes illustrated for the MDI-1-2-1(**BT**) system:


PPO
Δ
CO₂
CH₂=CH₂ + HN=C=O
Δ
Δ



Scheme I

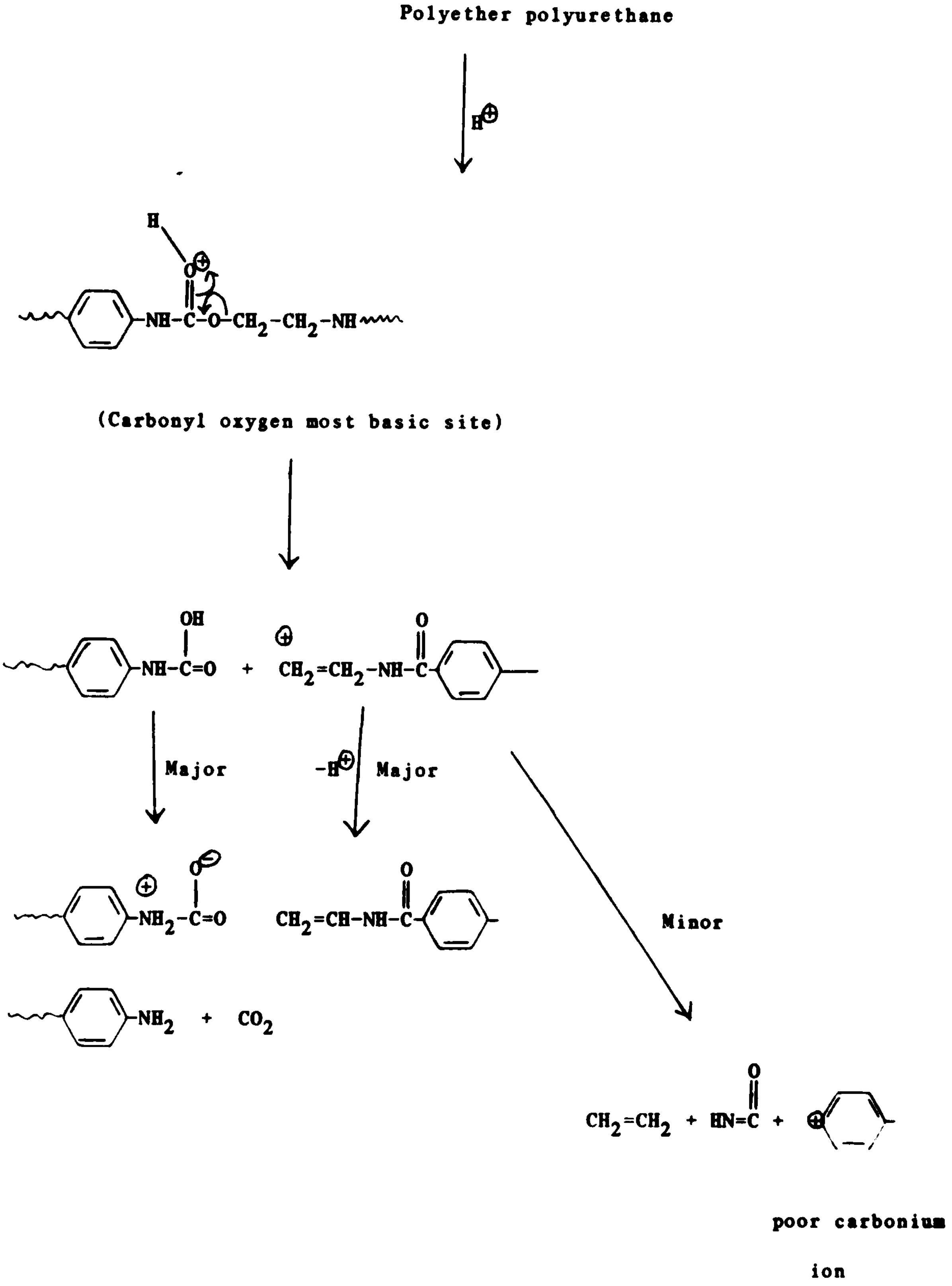
## Table IV

## First Stage TGA Weight Loss for Polyurethanes with MDI

| Polymer | % wt loss at 300°C<br>Found | Calculated |
|---|---|---|
| BT(1-3-2) | 15.5 | 15.1 |
| BT(1-2.5-1.5) | 15.5 | 15.2 |
| BT(1-2-1) | 12.5 | 12.5 |
| BT(1-1.67-0.67) | 8.1 | 8.2 |
| BI(1-3-2) | 15.5 | 18.1 |
| BI(1-2.5-1.5) | 15.5 | 15.2 |
| BI(1-2-1) | 12.8 | 12.8 |
| BI(1-1.67-0.67) | 8.5 | 8.2 |
| BI(1-1.5-0.5) | 6.0 | 6.12 |

In addition, the urethane group is susceptible to acid catalyzed decomposition. In Table III the values of $T_o'$, $T_{10}'$ and $T_{50}'$ obtained in the presence of 1% p-toluene sulfonic acid are given. The acid was added to the polyurethane solution and then the solvent removed by evaporation. The onset decomposition temperatures were lowered in all cases by amounts from 20° to 110°C. There was lowering of $T_{10}$ values also by the acid catalysis. The magnitude of lowering of $T_o$ by acid catalysis seem to be a function of the nature of the hard segment; with TDI $\Delta T_o$ is 53 to 54° for both **BT** and **BI** chain extender. In the MDI cases, the $\Delta T_o$ increases with the order of **BT** > **BI** > **B** ~ **BH** and there appears to be some effect of amount of hard segment in the polyurethanes.

The acid catalyzed decompositions are limited in scope as can be seen by the $T'_{50}$ values in Table II which are about the same as $T_{50}$ values obtained without acid. Figure 2 gives the comparison of the rate of isothermal decomposition of MDI-**BI** (1-2-1) polymer at 250°C with and without acid. The small effect of the acid may be explained by scheme II. Additional reasons are the volatile loss of the p-toluene sulfonic acid and the stability of polyether segments toward acid.


Polyether polyurethane
H⊕
(Carbonyl oxygen most basic site)
Major
-H⊕
Major
Minor
poor carbonium
ion

Scheme II

## Microscopy

According to the interpretation of $T_a$ values, it was proposed that the polyurethanes derived from MDI and **BT** are substantially phase separated, whereas those containing **BI** chain extenders may contain appreciable "mixing-in-domain" (vide supra). Films of polymers were solvent casted and studied with a polarizing microscope. The morphology depends upon the rate of removal of solvent. For illustrative purposes, Figure 2a shows the small spherulites formed by rapid removal of solvent from MDI-**BT** (1-3-2) polymer whereas much larger spherulites were obtained by slow evaporation of the polymer solution (Figure 3a). The spherulites exhibit sharp boundaries and are not appreciably affected by neating to 138°C and held there for 5 - 10 min (Figure 2b and 3b). The spherulite domains begin to decrease at 141°C (Figure 2c, 2d and 3C) which process continues until they disappear at 161°C. Table I gives $T_b$ for this polymer to be 138°C. But the heating rate of DSC is 20°C $min^{-1}$ which is much faster than the hot-stage microscope. Therefore, we can take 141°C as the true $T_b$ for the occurrence of "domain-boundary-mixing". At higher temperatures there may also be "mixing-in-domains". In fact, Figure 2e showed that though all the spherulites have disappeared at 160°C, phase separation remains because the polymer does not melt before composition.

In comparison, the MDI-**BI** (1-3-2) film display a distribution in Maltese cross domains. The smaller ones disappear at 127°C and the larger size ones persist and disappear at 161°C. These behaviors are consistent with the occurrence of "domain-boundary-mixing" at $T_b$ and total melting at $T_m$ given in Table I.

Domain separation is strongly dependent on the amount of hard segment in the polymer. For instance, when the hard segment content is 39% in MDI-BI (1-3-2) is lowered to 12% in (1-1.67-0.67), there was very low density of poorly formed Maltese cross domains. The structure of the chain extender in the hard segments also affect the spherulite formation. Figure 4 shows that for the MDI polyurethanes at the same wt % HS, the spherulite sizes decrease in the order BT > BI > B. In the case of TDI only small spherulites were formed with high percentage of hard segments.

### Mechanical Properties

The mechanical properties of several of the MDI poly(ether-*b*-urethanes) were studied. Figure 5 shows the stress-strain curves and the results are summarized in Table V.

The mechanical properties of MDI-BT copolymers are simple to interpret as the domain are clearly separated. The modulus, tensile and elongation of break increase monotonically with the increase of hard segment content. When the chain extender is BI the polyurethanes behave very differently from the BT polymers. With 38.9% HS the former has only one-fifth of the modulus and $\sigma_b$ and about one-half of $\varepsilon_b$ of the latter polymer. For the BI (1-2.5-1.5) copolymer it is transitional in behavior to materials which behave as uncrosslinked elastomers at lower wt % HS. The BI (1-1.67-0.67) material is virtually without much mechanical strength. This is also true for the butadiol extended polyurethanes (Table V). Therefore, when there is either "domain-boundary-mixing" or "mixing-in-domain" the hard segment domains act either as weak crosslinks or not at all.

Table V
Mechanical Properties of Polyurethanes from MDI

| Polymer | Wt % HS | Domain Size, μ | E, MPa | $\sigma_b$, MPa | $\varepsilon_b$, % |
|---|---|---|---|---|---|
| **BT**(1-3-2) | 38.9 | 20 | 4.34 | 29.0 | 714 |
| **BT**(1-2.5-1.5) | 33.4 | 23 | 2.90 | 12.8 | 530 |
| **BT**(1-2-1) | 27.3 | 20 | 2.57 | 2.9 | 324 |
| **BT**(1-1.67-0.67) | 22.7 | 17 | 0.82 | 1.6 | 149 |
| **BI**(1-3-2) | 38.9 | 15 | 0.75 | 8.6 | 420 |
| **BI**(1-2.5-1.5) | 33.4 | 13 | 0.26 | 3.3 | 501 |
| **BI**(1-2-1) | 27.3 | 11.7 | 1.5 | 0.74 | 1720 |
| **BI**(1-1.67-0.67) | 22.7 | 10 | 1.7 | 0.081 | 2400 |
| **B**(1-3-2) | 31.9 | 7.0 | 15.4 | 6.4 | 375 |
| **B**(1-2-1) | 22.8 | 5.0 | 1.8 | 0.3 | 640 |
| **BB**(1-2-1) | 25.9 | 13 | 5.14 | 1.5 | 72 |

## Conclusions

Systematic studies of PPO polyurethanes obtained with different kinds of diisocyanate and chain extenders show strong structure property relationships reflecting the degree of microphase separation. For both symmetric MDI and BT system, the $T_{\underline{a}}$ is low and independent of wt % HS, there is mixing at domain boundary at $T_{\underline{b}}$ = 141°C, does not melt before decomposition, displaying abundance of spherulites, and the mechanical properties are consistent with a thermoplastic elastomers with strong physical crosslinks. Change of the chain extender alone to asymmetric BI causes a large decrease in hard segment crystallization because of "mixing-in-domain". $T_{\underline{a}}$ is raised with increasing amount of chain extender, disappearance of small spherulite at $T_{\underline{b}}$ and total melting ant $T_{\underline{m}}$. With HS of less than 30 wt %, the polymers act as non-crosslinked elastomer. In the case of butandiol chain extension, there is believed to be substantial "domain-boundary-mixing", and high $T_{\underline{a}}$ of -36°C. At 70°C there is mixing of domains. $T_{\underline{m}}$ is very low at about 138°. Similar properties are manifest for polyurethanes obtained with asymmetric TDI regardless whether the chain extender is symmetric (BT) or asymmetric (BI). The polyurethanes of HDI lie somehwere between the above two types of polymers probably even though HDI is symmetric, the flexible hexamethylene linkages significantly affect its properties.

Thermal decomposition begins initially at temperatures between 200° and 300°C. The PPO segments decompose at much higher temperatures.

## ACKNOWLEDGEMENT

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## Captions for Figures

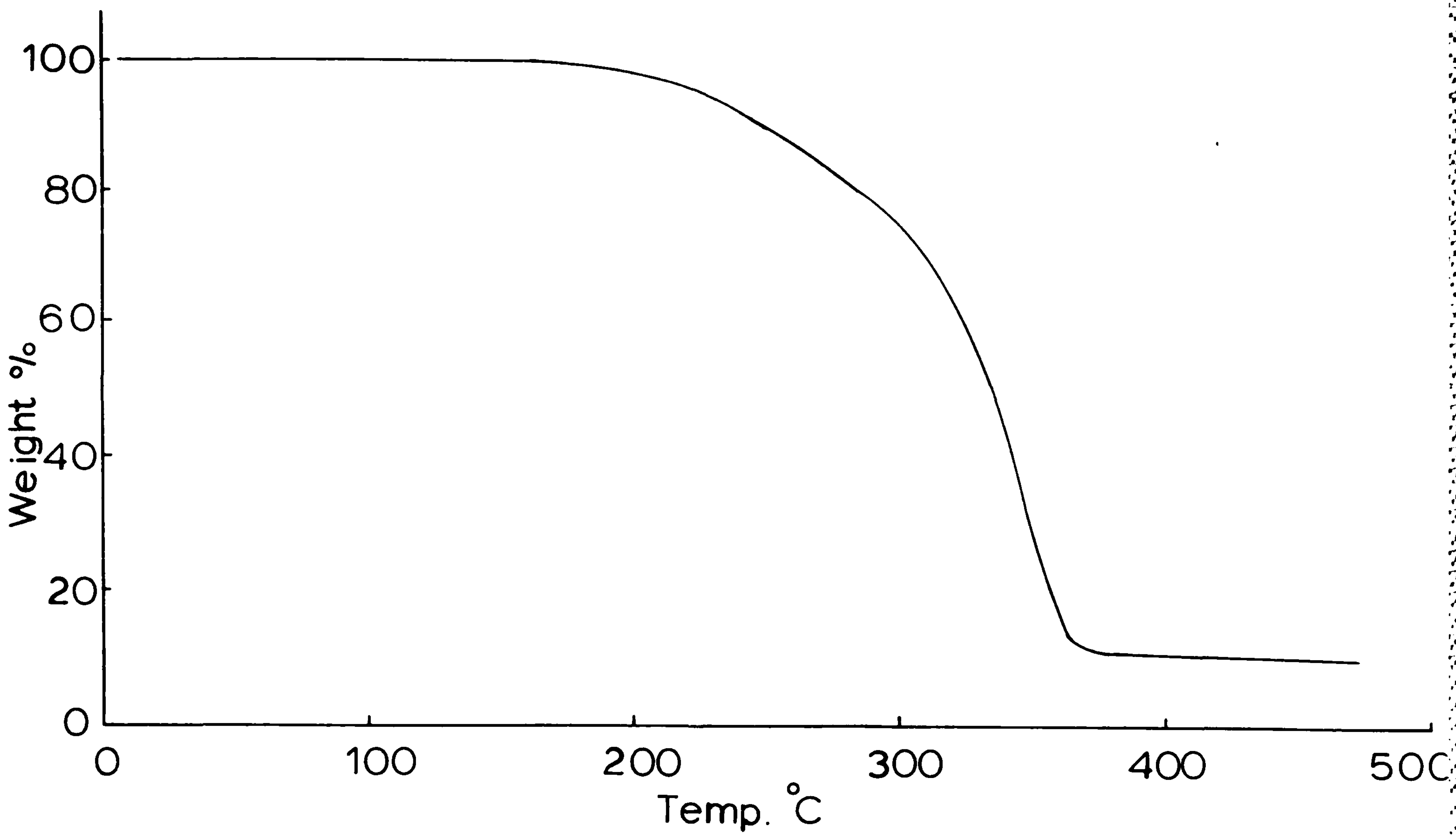
**Figure 1.** Typical TGA curve for MDI-BI (1-2-1) polyether polyurethane. Scan rate is 20°/min

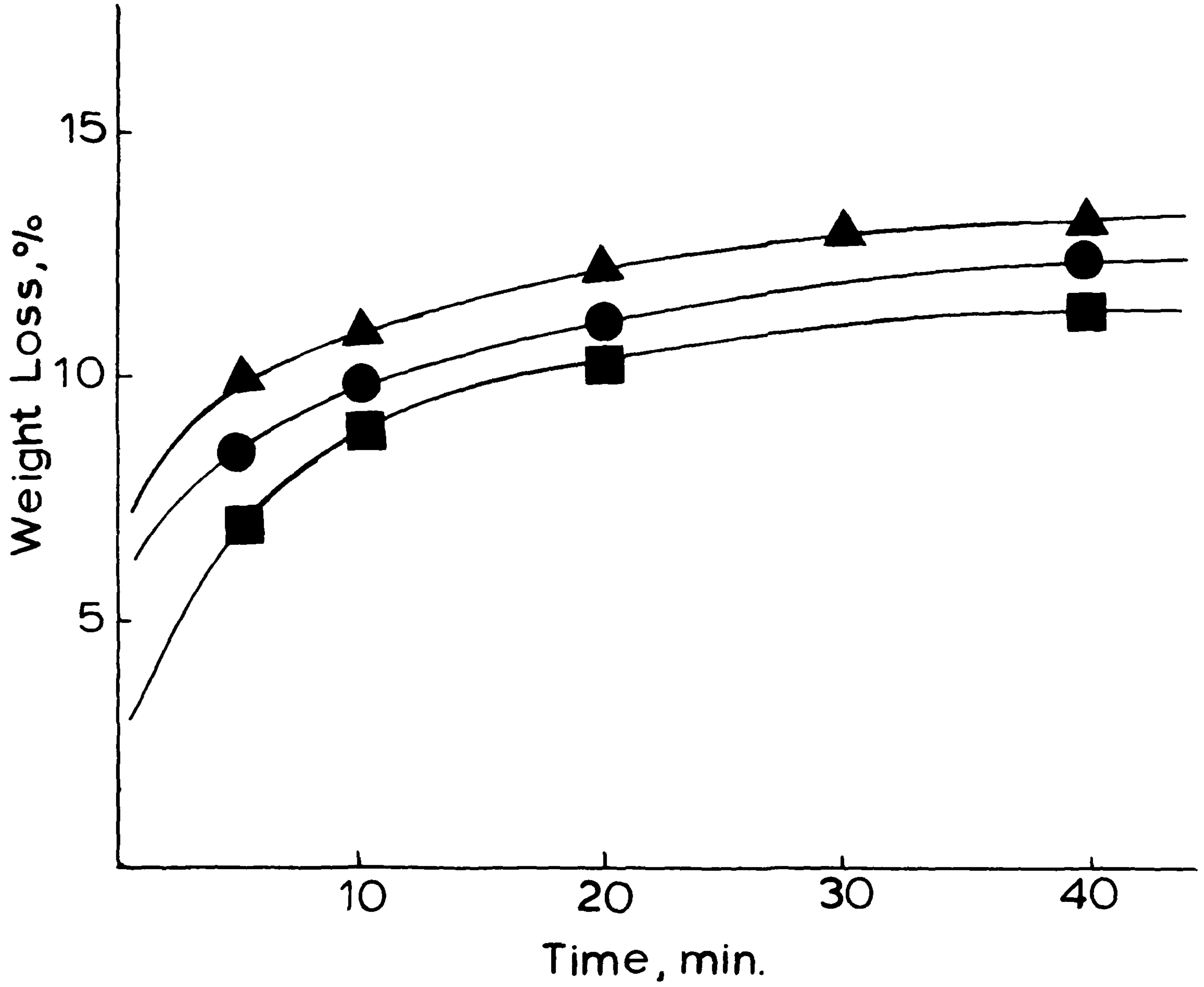
**Figure 2.** Isothermal decomposition of MDI-BI (1-2-1) polymer at 250°C with wt % of p-toluene sulfonic acid: (a) 0; (b) 1%; (c) 2%.

**Figure 3.** Polarized photomicrographs of MDI-BT (1-3-2) polymer prepared with rapid solvent evaporation, magnification x 100: (a) 25°C; (b) 138°C for 5 min; (c) 141°C for 3 min; (d) 141°C for 7 min; (e) 160°C. Marker is 100 micron.

**Figure 4.** Polarized photomicrograph of MDI-BT (1-3-2) polymer prepared with slow solvent evaporation magnification x 100: (a) 25°C; 138°C for 10 min; (c) 141°C for 5 min. Marker is 100 micron.

**Figure 5** Variation of spherulite sizes wt % HS for different MDI polyurethanes with chain extenders: (Δ BT; (O) BI; (o) B.


Weight %
100
80
60
40
20
0
0
100
200
300
400
500
Temp. °C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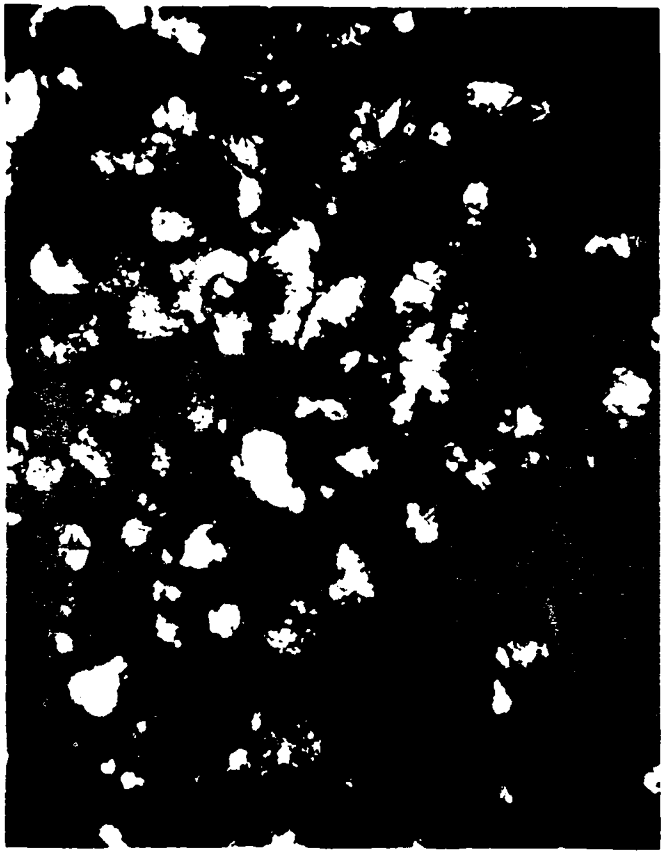
15
10
5
10
20
30
40
Time, min.


100μ

[illegible]

[illegible]

[illegible]

Figure 3c

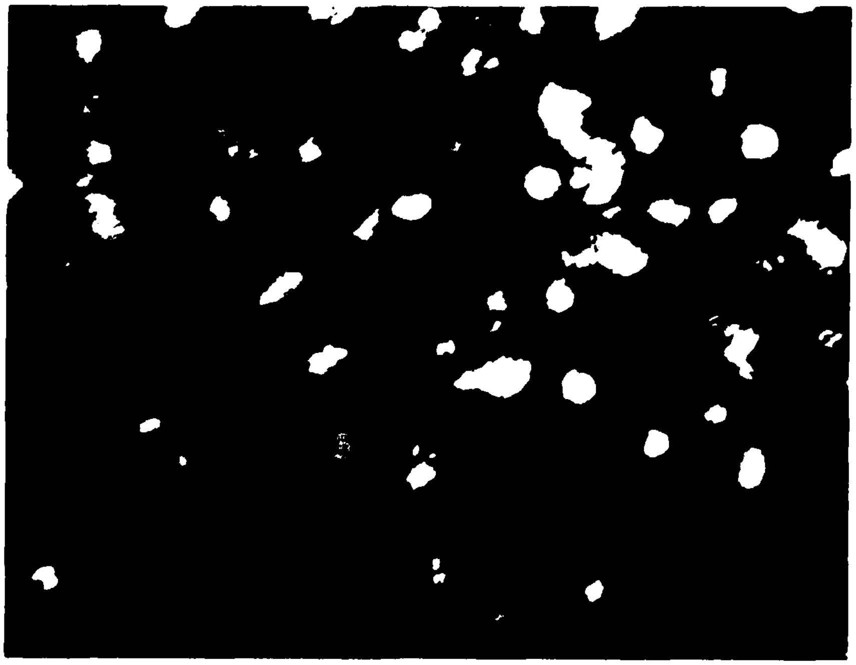


Figure 3d

Figure 3e

Figure 4a

Figure 4b

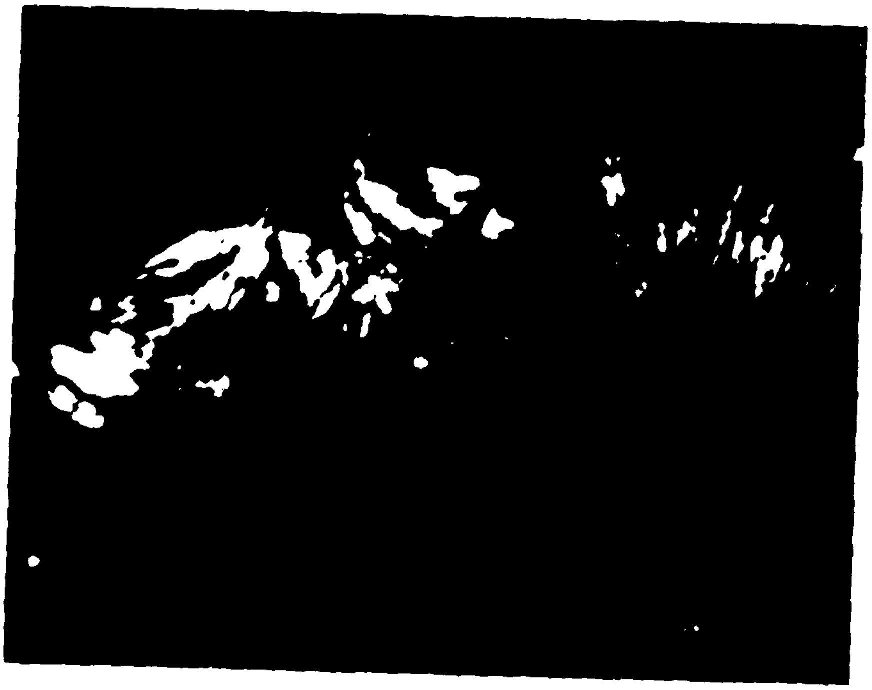


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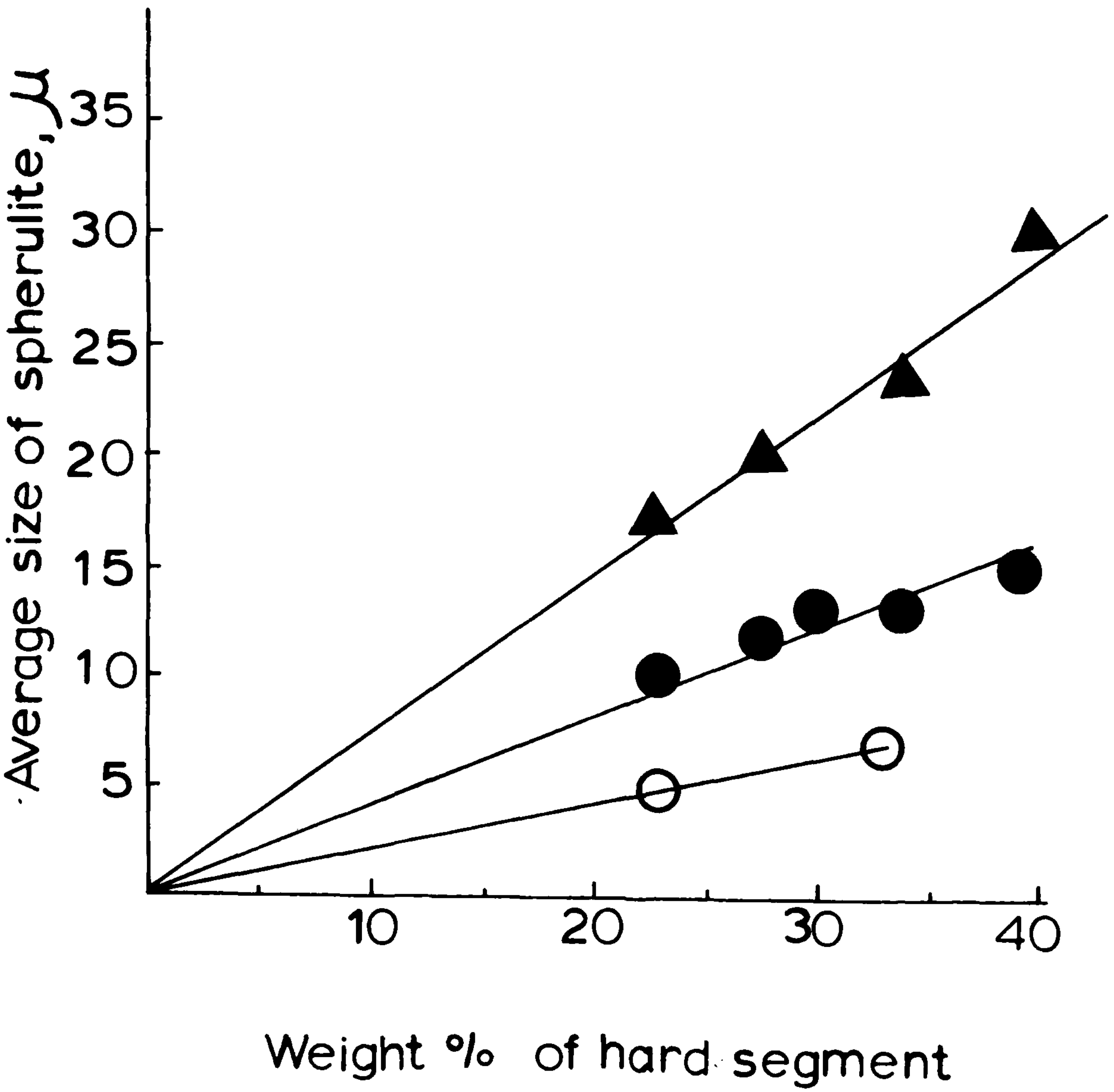
Figure 4c


Average size of spherulite, μ
35
30
25
20
15
10
5
10
20
30
40
Weight % of hard segment