

# Polyurethane ionomers: effects of emulsification on properties of hexamethylene diisocyanate-based polyether polyurethane cationomers

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Hexamethylene diisocyanate-based polyether polyurethane cationomer solutions are prepared and then emulsified by adding water. The properties of films cast from solutions and emulsions are studied using infra-red spectroscopy, dynamic mechanical analysis, thermogravimetric analysis, differential scanning calorimetry, wide-angle X-ray diffraction and tensile elongation testing. It is found that the use of the asymmetric chain extender, *N*-methyl-diethanolamine, can also lead to a polyurethane (PU) with detectable ordering in the hard domains, as in the PU with a symmetric chain extender such as 1,4-butanediol. After quaternization with glycolic acid, the PU cationomers have increased tensile modulus and decreased elongation and tensile strength. These can be attributed to the Coulombic interaction between two neighbouring hard segments and to disruption of the ordering in the hard domains. Emulsification of the PU ionomer solution can lead to slightly increased phase mixing and decreased tensile properties. During the emulsification, conductivity and viscosity variations show that water is first adsorbed on the surface of the hard-segment microionic lattices and then enters successively into the disordered hard domains, the short-range and the long-range hard domains.

(Keywords: hexamethylene diisocyanate; poly(tetramethylene oxide); *N*-methyl-diethanolamine; glycolic acid; emulsification; ordering)

## INTRODUCTION

Polyurethane (PU) ionomers can be prepared by incorporation of a chain extender containing an amino group with NCO-terminated PU and subsequent modification with an ionic component<sup>1</sup>. There are three types of PU ionomer: (1) cationomers, formed by a tertiary amine reacting with alkyl halide; (2) anionomers, formed by a secondary amine reacting with a sultone or lactone; and (3) zwitterionomers, formed by a tertiary amine reacting with a sultone to form a quaternary ammonium sultone. Owing to the use of a chain extender having asymmetrical structure and to the presence of the ionic component, PU ionomers exhibit considerable differences in morphology and physical properties in comparison to their respective conventional PUs involving the same polyol (or polyamine) and diisocyanate. The tensile strength and modulus of a zwitterionomer are higher than its corresponding conventional PU, whereas its ultimate per cent elongation remains about the same<sup>2,3</sup>. For a conventional PU, various extents of order coexist in the hard segments, involving disorder, short-range order, long-range order and microcrystalline order<sup>4,5</sup>. In the zwitterionomers investigated by Cooper and coworkers<sup>2,6-10</sup>, no disorder and orders were observed except in one case, which involves hard-segment crystallinity. In the anionomer involving a sultone ion, only disorder

and crystalline hard segments were observed<sup>9</sup>. For the cationomer, no study involving order in the hard segments has so far been found in the open literature.

By addition of water to an organic solution of the ionomer and then removal of the organic solvent, a so-called PU emulsion can be obtained. The PU emulsion can be cast into a film in the same way as the PU solution but without pollution. However, studies on the morphologies and physical properties of films cast from emulsions are limited. Lorenz *et al.*<sup>11,12</sup> reported tensile strengths of films cast from emulsions without comparison with those of films cast from solutions.

The diisocyanates used in the work mentioned above are 4,4'-diphenylmethane diisocyanate (MDI) for zwitterionomers and anionomers<sup>2,6-10</sup> and toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) for anionomers and cationomers<sup>11,12</sup>. However, the structure-property relationship of a PU ionomer based on HDI has not been reported in the literature, despite the fact that HDI is used extensively in PU synthesis.

In this work, films cast from solutions and emulsions of polyether PU cationomers based on HDI are compared for any differences in structures and properties using thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), infra-red spectroscopy (i.r.), dynamic mechanical analysis, stress-strain testing and wide-angle X-ray diffraction (WAXD). In addition, the phase inversion mechanism during emulsification is studied based on conductivity and viscosity measurements.

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## EXPERIMENTAL

### Materials

Hexamethylene diisocyanate (HDI) and glycolic acid crystals of extra pure grade (Merck Chemical Co.), bromophenol blue indicator (Wako Chemical Co.), and dibutyltin dilaurate and *N*-methyldiethanolamine (MDEA) (Toyo Kasei Co., extra pure) were used as received. Poly(tetramethylene oxide) (PTMO) of molecular weight 2000 (Du Pont Chemical Co.) was further dehydrated under vacuum at 50°C for 24 h. Methyl ethyl ketone (MEK) (Merck Chemical Co., 99.5% pure) was dried by distillation with P<sub>2</sub>O<sub>5</sub> and then stored over 4 Å molecular sieves before use.

### Synthesis of polyurethane cationomer solutions

PU prepolymer was prepared at 70–75°C under a nitrogen atmosphere in a stirred glass reaction kettle with reflux condenser. HDI was charged into the kettle first and heated up to 70–75°C. Then an appropriate amount of PTMO in MEK was added slowly such that one of the two hydroxyl groups in each polyol molecule could react with one molecule of HDI to yield prepolymers of various NCO/OH ratios. Dibutyltin dilaurate (as catalyst) was added at the beginning of the polymerization. The reaction was allowed to proceed until the theoretical isocyanate content was reached as determined by the di-*n*-butylamine method<sup>13</sup>.

The prepolymer was then diluted to 15 wt % with MEK to lower the rate of heat generation and to avoid a substantial increase in viscosity during the subsequent chain extension reaction. An appropriate amount of MDEA in MEK was added slowly to the diluted prepolymer solution at 70–75°C. The reaction was continued until all the –NCO groups were reacted as confirmed by the disappearance of i.r. absorption at 2270 cm<sup>-1</sup>. An appropriate amount of glycolic acid in MEK was added to the polyether PU solution. The mixture was stirred at 65°C for 1 h to allow quaternization. The degree of ionization was dependent on the amount of glycolic acid added.

### Emulsifications

The deionized water was added slowly under constant agitation to the polyether PU cationomer solution in MEK having a solid content of 10 wt %, into which a conductivity probe was immersed to monitor the conductivity variation. As the conductivity of the solution reached a constant level, indicating that the phase inversion process was completed, the addition of water was stopped.

### Film preparations

Films for physical testing were prepared by pouring the solution or emulsion into a Teflon mould. After standing at room temperature for 4 days to allow evaporation of the solvent or water, it was then vacuum dried at 60°C for 48 h in order to remove completely the residual solvent or moisture.

Samples were designated in the following way: for example, H-1-6-5-1.0-20°C means one mole of PTMO, six moles of HDI, five moles of MDEA and 1.0 mole ratio of glycolic acid to MDEA are used, and the dispersion temperature is 20°C; the first letter 'H' refers to HDI.

### Measurements

During the emulsification, the conductivity of the solution was measured using a conductivity meter from Crison Instrument Co. and the solution viscosity was determined using a Brookfield Synchro-Lectric Viscometer with spindles LVT no. 1–4 at the dispersion temperature, 20°C.

The tensile properties were measured at room temperature using a Shimadzu Universal Testing Machine, Model 502, with a cross-head speed of 50 mm min<sup>-1</sup>. The dumbbell-type specimen has dimensions of 25 mm wide at each end, 0.1–0.4 mm thick and 10 mm wide at the neck (JIS K6301 method).

Differential scanning calorimetric (d.s.c.) thermograms over the temperature range 50–300°C were recorded using a Perkin–Elmer DSC-2C at a heating rate of 20°C min<sup>-1</sup>, sensitivity of 5 mcal s<sup>-1</sup>, under nitrogen purging. The weight of each sample was 5 ± 0.05 mg.

Thermogravimetric analysis (t.g.a.) over the temperature range 40–400°C was carried out using a Perkin–Elmer TGS-2 with a heating rate of 20°C min<sup>-1</sup> under nitrogen purging. The weight of each sample was 4–5 mg.

Infra-red (i.r.) spectra were recorded using an i.r. spectrophotometer, Model 983 from Perkin–Elmer Co., at a resolution of 3 cm<sup>-1</sup>.

Dynamic mechanical properties over the temperature range of –150 to 120°C were measured using a computer-controlled Dynamic Rheovibron DDV-II-EA from Toyo Baldwin Co., with a frequency of 110 Hz, heating rate of 2°C min<sup>-1</sup> and temperature interval of 2°C. Precision of temperature reading was ±0.1°C.

Wide-angle X-ray diffraction (WAXD) measurements were made using a Rigaku Model D/Max-II diffractometer. The X-ray beam was nickel-filtered Cu K<sub>α</sub> (λ = 0.1542 nm) radiation from a sealed tube operated at 30 kV and 10 mA. Data were obtained from 5° to 40° (2θ) at a scan rate of 4° min<sup>-1</sup> with a smoothing time constant of 4 s.

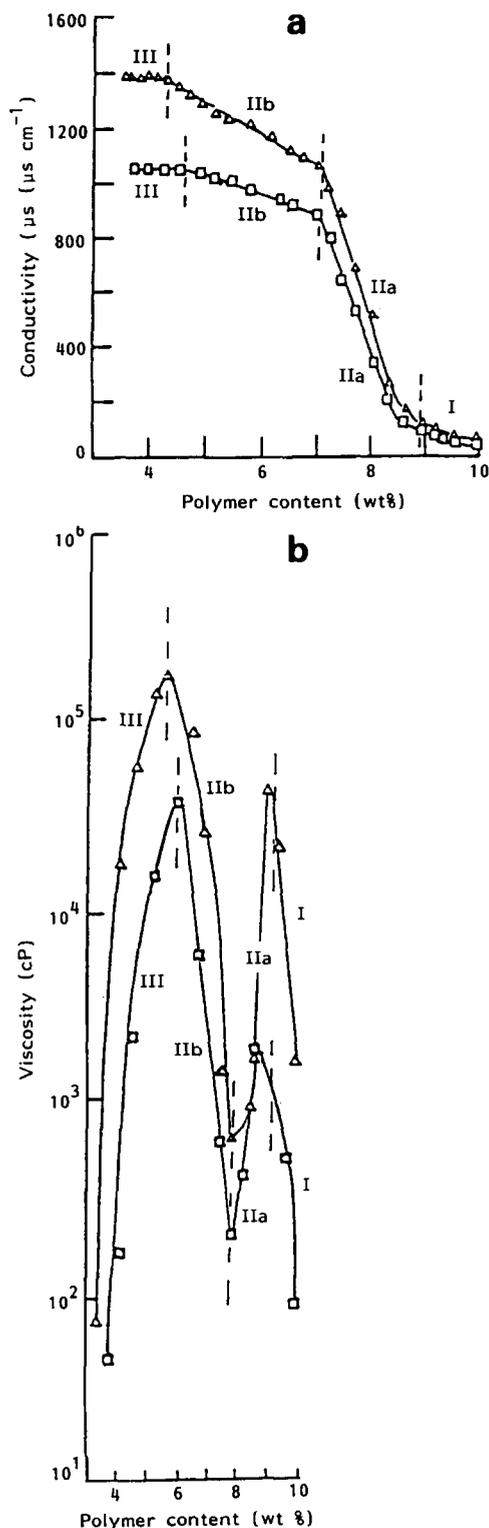
## RESULTS AND DISCUSSION

### Conductivity and viscosity measurements

The conductivity and viscosity variations of H-1-6-5 series solutions during addition of water at the dispersion temperature, 20°C, are shown in *Figure 1*. The inversion process can be clearly divided into three regions, as marked on the figure.

In region I, the solution conductivity curves are slightly concave upwards and the solution viscosity increases sharply. These indicate that, as water is added slowly to the ionomer solution, the water is adsorbed by the ionic groups situated on the surface of the hard-segment microionic lattices, causing dissociation with their counterions according to Dieterich *et al.*<sup>1</sup> In addition, the water also enters into parts of the disordered hard domains, since the *T*<sub>gh</sub> of the ionized films cast from solution are about –15.2 to –17.3°C as determined from dynamic mechanical measurements (see later section), much lower than the present dispersion temperature. The sharp increase in viscosity can be attributed to chain extension of the hard segments in the interior of the disordered hard domains.

In region IIa, as more water is added, the water molecules first enter into the short-range order portion of the hard-segment microionic lattices. From d.s.c.



**Figure 1** The (a) conductivity variations and (b) viscosity variations of the H-1-6-5 series solutions during water addition at the dispersion temperature, 20°C: (□) H-1-6-5-0.7; (△) H-1-6-5-1.0

measurements (see later section), the unionized film cast from solution has two endotherm peaks due to the presence of short- and long-range orders in the hard domains, but the ionized film has the long-range endotherm peak only. This result indicates that the short-range order is destroyed, or reduced to an extent undetectable by d.s.c., by the ionization. The solution viscosity increases continuously to reach a maximum, while the conductivity increases concave upwards and

then linearly, indicating that the short-range order hard segments still exist. Further addition of water gives a sharp decrease in viscosity, indicating that dissociation of all the short-range order hard-segment microionic lattices is complete.

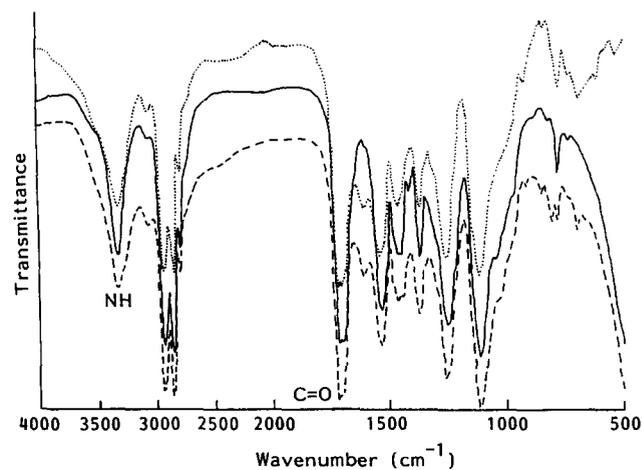
Continuous addition of water (region IIb) makes the viscosity increase sharply again to another maximum; while the conductivity also increases until a constant level is reached, indicating entry of the water into the long-range order hard-segment microionic lattices. This consideration can also be manifested by significant lowerings of the two characteristic peak temperatures of the long-range ordered domains due to phase inversion (to be discussed later). For example, for H-1-6-5-0.7 dispersed at 20°C, the emulsion-cast film has lower-temperature peak and higher-temperature peak of the long-range ordered hard segments 14°C and 13°C lower than the solution-cast film as determined from the d.s.c. measurements (see later section).

In region III, the phase inversion is complete, the solution viscosity drops sharply and the solution conductivity remains almost constant.

#### Infra-red spectroscopy

The i.r. spectra of films cast from solution and emulsion are shown in Figure 2. For the unionized films, the region of the NH band (3000–3500  $\text{cm}^{-1}$ ) has a peak at 3340  $\text{cm}^{-1}$  due to hydrogen-bonded NH groups, but the peak at 3460  $\text{cm}^{-1}$  due to free NH groups is not present, indicating that the NH group appears to be completely hydrogen-bonded. While the C=O band in the region of 1650–1750  $\text{cm}^{-1}$  is split into two peaks, that centred at 1703  $\text{cm}^{-1}$  is due to bonded C=O, and that at 1730  $\text{cm}^{-1}$  to free C=O; both peaks have about the same intensity. Since most of the NH groups are hydrogen-bonded while some of the C=O groups are still free, these indicate that the NH groups must also bond to the ether groups of the soft segments in addition to the C=O groups in the urethanes<sup>14</sup>.

For the ionized films (Figure 2), the NH peak in the region of 3000–3500  $\text{cm}^{-1}$  shifts downwards. The extent of shifting increases with the degree of ionization, and is downward by 30  $\text{cm}^{-1}$  as the ionic content is 1.0. However, the absorption of free C=O increases slightly



**Figure 2** I.r. spectra of the H-1-6-5 series materials: (—) H-1-6-5-0; (---) H-1-6-5-1.0; (····) H-1-6-5-1.0-20°C

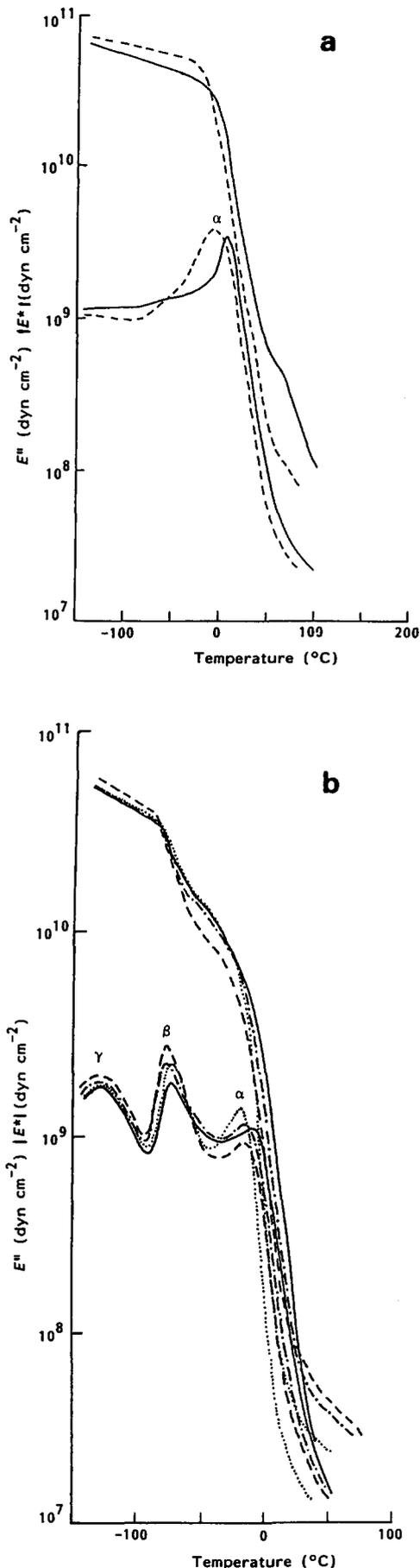


Figure 3 (a) Dynamic mechanical analysis of the HDI pure hard-segment materials: (—) H-hard-0; (---) H-hard-1.0. (b) Dynamic mechanical analysis of the H-1-6-5 series materials: (—) H-1-6-5-0; (---) H-1-6-5-0.7; (---) H-1-6-5-1.0; (····) H-1-6-5-1.0-20°C

after the ionization. Therefore some of the NH groups previously bonded to the C=O of the urethane must switch to bond with the stronger proton accepting group, COO<sup>-</sup>.

For the emulsion-cast film, the absorption frequency of the NH group is the same as that of the solution-cast films. But the absorbance of the free C=O at 1730 cm<sup>-1</sup> of the emulsion-cast film is more intense than that of the solution-cast films. This indicates that a disruption of the ordered packing arrangement in the hard domains occurs during the dispersion process.

Dynamic mechanical analysis

The dynamic mechanical measurements of films cast from solution and emulsion are shown in Figure 3 and their transition temperatures determined from the maxima of the loss moduli, E'', are listed in Table 1. Three peaks in the E'' curves are observed. The beta peak is taken as the glass transition temperature of the soft domain (T<sub>gs</sub>). The presence of the gamma peak (below the beta peak) between -127°C and -130°C can be attributed to the relaxation process involving the local motion of the methylene sequences of the polyether segments<sup>15</sup>. The alpha peak is taken as the glass transition temperature (T<sub>g</sub>) of the disordered hard segments (T<sub>gh</sub>).

For the HDI pure hard-segment films cast from solution, there is only one maximum in the E'' curve (Figure 3a and Table 1). Upon ionization, this peak drops by 15.9°C and is broadened, indicating that the ionization can disrupt the order of the hard segments.

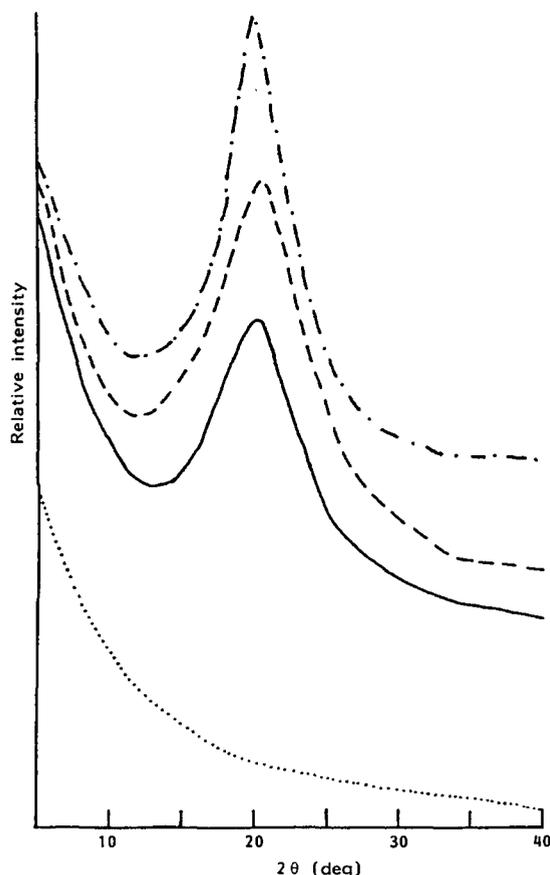
For the solution-cast films, both T<sub>gs</sub> and T<sub>gh</sub> drop about 1.9 and 4°C respectively after the ionization, but further increase of the ionic content does not give a further drop for T<sub>gs</sub>, but does for T<sub>gh</sub> (Figure 3b and Table 1). These results indicate that the ionization can lead to an increased disordering of the hard segments in the hard domains, and give no increase in phase separation.

For H-1-6-5-20°C materials, T<sub>gs</sub> shifts 1.9°C higher than the respective solution-cast film, H-1-6-5-1.0, while T<sub>gh</sub> drops by 0.2°C. The level of tensile modulus in the entire temperature range investigated also decreases slightly after emulsification. This result indicates that the emulsification leads to a slight increase in phase mixing. Note also that the alpha peaks are appreciably sharper than that of the solution-cast film. This is due to the increased amount of disordered hard domains resulting because parts of the hard segments of long-range order are converted into disordered. This interpretation can be supported by the fact that water can enter into the hard domains with long-range order due to the significantly lower T<sub>gh</sub>.

Table 1 The characteristic peaks determined from dynamic mechanical curves of films cast from solution and emulsion

Sample	gamma peak (°C)	beta peak (°C) T <sub>gs</sub>	alpha peak (°C) T <sub>gh</sub>
H-hard-0 <sup>a</sup>	—	—	6.7
H-hard-1.0 <sup>a</sup>	—	—	-9.2
H-1-6-5-0	-129.4	-73.3	-11.3
H-1-6-5-0.7	-129.4	-75.2	-15.2
H-1-6-5-1.0	-129.4	-75.2	-17.3
H-1-6-5-1.0-20°C	-129.1	-73.3	-17.5

<sup>a</sup>H-hard has the ratio of HDI/MDEA, 1/1 by mole



**Figure 4** Angular dependence of WAXD of the H-1-6-5 series materials: (—) H-1-6-5-0; (---) H-1-6-5-1.0; (-·-·-) H-1-6-5-1.0-20°C; (····) baseline (or blank)

#### Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) curves of films cast from solution and emulsion are shown in *Figure 4*. No evidence of either hard- or soft-segment crystallinity is found in the WAXD patterns. Only a single, diffuse scattering peak with a maximum intensity near 20° (2θ) was observed, indicating an amorphous and insufficient order arrangement of the chain segments<sup>16</sup>. The reason is that the chain extender has a side group (-CH<sub>3</sub>) which leads to an irregular packing of the hard segments.

#### Thermogravimetric analysis

T.g.a. curves of films cast from solution and emulsion are shown in *Figure 5*. These curves show that the ionized films lose weight in three stages, but for the unionized films the first stage is absent. The onset temperature and weight loss of each stage are summarized in *Table 2*.

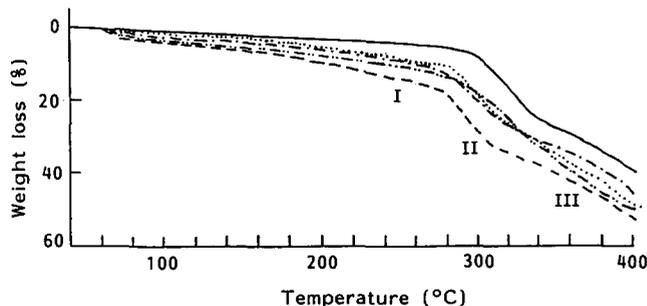
For the solution-cast films, *Table 2* shows that the per cent weight losses in stages I and II are also about equal to the weight per cent of the incorporated acid and chain extender respectively. The onset temperature of stage II drops upon ionization, indicating that ionization can disrupt the ordering in the hard domains, allowing thermal decomposition of chain extender segments at a lower temperature. This result is in agreement with those from i.r. and dynamic mechanical measurements.

#### Differential scanning calorimetry

D.s.c. curves for films cast from solution and emulsion are shown in *Figure 6*. The temperatures of the characteristic peaks of all samples are listed in *Table 3*.

For the H-1-6-5 series films cast from solution, two major endotherm peaks are found in the temperature range 50–310°C (*Figure 6*). Peak I temperature of the unionized films (H-1-6-5-0) is 80°C, but for the ionized samples this peak becomes rather flat. Peak II is split into two: the lower-temperature peak (ltp) is about 26–47°C lower than the higher-temperature peak (htp). The htp decreases slightly but ltp increases with the degree of ionization. For the HDI pure hard-segment films cast from solution (*Figure 6b*), peak I temperature increases and both htp and ltp of peak II decrease with degree of ionization. In addition a new peak in between the htp and ltp is generated. The area of peak II increases after the ionization.

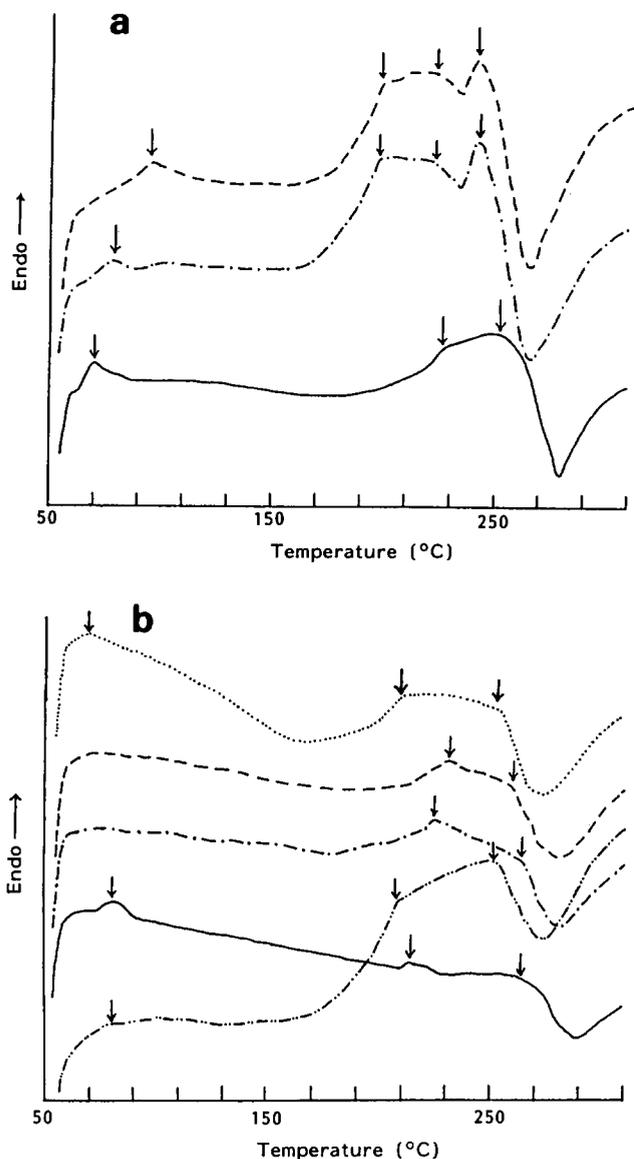
First, let us assign physical meanings for peaks I and II. For the ionized and unionized films, peak I temperatures of d.s.c. curves are in the range 70–94°C, while  $T_g$  of hard segments ( $T_{gh}$ ) is -17.3°C (for H-1-6-5-1.0) as determined from the dynamic mechanical analysis above. In addition, the peak I temperature is close to the dissociation temperature of the hard-segment short-range order (about 70°C) in unannealed conventional PU (composed of MDI/PTMO/1,4-butane diol)<sup>4</sup>. Thus, peak I of d.s.c. cannot be due to dissolution of the amorphous hard segments (or glass transition) or evolution of the acid (occurred in the range 172–274°C) but can be reasonably assigned to the short-range order of the hard segments. For the physical meaning of peak II, the peak exists for both the ionized and unionized systems. The htp is 258°C for H-1-6-5-1.0, while the onset weight loss temperature of stage II in the t.g.a. curves, 274°C, is higher. In addition, the htp is higher than both the temperature at maximum ratio of weight loss in stage I of the t.g.a. curve (*Figure 5*) and the dissociation temperature of the hard segments with long-range order (130–155°C) in the unannealed conventional PU composed of



**Figure 5** T.g.a. curves of the H-1-6-5 series materials: (—) H-1-6-5-0; (---) H-1-6-5-0.7; (-·-·-) H-1-6-5-1.0; (-·-·-) H-1-6-5-0.7-20°C; (····) H-1-6-5-1.0-20°C

**Table 2** The characteristic values of the t.g.a. curves of films cast from solution and emulsion

Sample	Amount added (wt%)		Onset temperature of each stage (°C)			Found weight loss (%)	
	Acid	MDEA	I	II	III	Stage I	Stage II
H-1-6-5-0	—	16.75	—	298	330	—	19.0
H-1-6-5-0.7	6.86	15.60	172	274	314	6.0	18.0
H-1-6-5-0.7-20°C	—	—	177	292	326	8.5	17.0
H-1-6-5-1.0	9.52	15.15	173	275	312	10.0	18.0
H-1-6-5-1.0-20°C	—	—	173	286	321	9.0	17.0



**Figure 6** (a) D.s.c. curves of the HDI pure hard-segment materials: (—) H-hard-0; (---) H-hard-0.7; (-·-) H-hard-1.0. (b) D.s.c. curves of the H-1-6-5 series materials: (—) H-1-6-5-0; (---) H-1-6-5-0.7; (-·-) H-1-6-5-1.0; (···) H-1-6-5-0.7-20°C; (···) H-1-6-5-1.0-20°C

MDI/PTMO/1,4-butane diol<sup>5</sup>. Thus, htp is not due to evolution of the acid or decomposition of the main chains, but can be assigned to the long-range order of the hard segments. The presence of ltp in peak II after the ionization can be attributed to dissociation of the hard segments with less ordered long-range order. Since acid evolution occurs in the temperature range of peak II, the increase in area of peak II can be attributed to the evolution of the acid.

For the H-1-6-5 series films cast from emulsion, peak I, which is rather broad for the solution-cast films, now becomes larger as the ionic content increases. For peak II, the htp and ltp are significantly lower than those of the solution-cast films by 3–13°C and 14–20°C respectively. The peak height ratio of the ltp to htp decreases after the emulsification. The total area of peaks I and II increases after emulsification. These observations indicate that the water already enters into the hard domains with short- and long-range orders during the emulsification, and that the degree of order in the hard domains decreases.

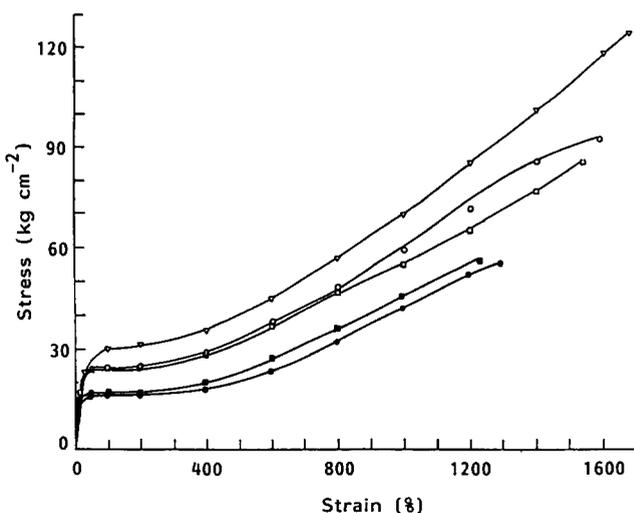
### Tensile properties

The tensile properties of films cast from solution and emulsion are shown in Figure 7. The tensile strength, elongation at break and tensile modulus are listed in Table 4. For the solution-cast films, upon ionization the tensile strength and elongation at break decrease. This is because the ionization decreases the order of the hard segments. But, the tensile modulus of the ionized film is higher than that of the unionized film, because the ionization increases the cohesion in the hard domains. Since the tensile elongation curves are concave upwards (Figure 7) and sample whitening occurs during

**Table 3** The characteristic peaks determined from d.s.c. curves of films cast from solution and emulsion

Sample	Peak I (°C)	Peak II <sup>a</sup> (°C)	
		Ltp	Htp
H-1-6-5-0	80	214	261
H-1-6-5-0.7	—	224	264
H-1-6-5-0.7-20°C	78	210	251
H-1-6-5-1.0	—	232	258
H-1-6-5-1.0-20°C	68	212	255
H-hard-0	70	226	249
H-hard-0.7	89	196; 223	241
H-hard-1.0	94	197; 222	240

<sup>a</sup> Ltp and htp refer to the lower- and higher-temperature peaks of peak II respectively



**Figure 7** Stress-strain curves of the H-1-6-5 series materials: (▽) H-1-6-5-0; (○) H-1-6-5-0.7; (□) H-1-6-5-1.0; (●) H-1-6-5-0.7-20°C; (■) H-1-6-5-1.0-20°C

**Table 4** The characteristic values of the tensile elongation curves of films cast from solution and emulsion

Sample	Tensile strength (kg cm <sup>-2</sup> )	Elongation (%)	Tensile modulus (kg cm <sup>-2</sup> )
H-1-6-5-0	125	1635	77
H-1-6-5-0.7	93	1583	145
H-1-6-5-0.7-20°C	56	1294	112
H-1-6-5-1.0	86	1537	175
H-1-6-5-1.0-20°C	57	1245	132

deformation, crystallization in the soft-segment phase during deformation evidently occurs. This result reflects the fact that the ordered hard domains must be aggregated so tightly as to act as 'crosslinks'. Upon ionization, the tensile strength of HDI series materials decreases, owing to the significant disruption of the order in the hard domains, while the tensile modulus increases and the elongation at break decreases, owing to the increased cohesion in the hard domains.

For the films cast from emulsion, the tensile strength and modulus and elongation at break are all lower than those of the solution case. This can be attributed to the lower  $T_{gh}$ , allowing the entry of water into the disordered and ordered hard domains and therefore causing disruption of the order.

## CONCLUSIONS

For the NCO-terminated polyurethane (PU) prepolymer, chain extension by use of the asymmetric chain extender, *N*-methyldiethanolamine, can also lead to a PU with detectable order in the hard segments as in the PU with a symmetric chain extender such as 1,4-butanediol. After quaternization with glycolic acid, the PU cationomers have increased tensile modulus and decreased elongation at break and tensile strength. These can be attributed to the ionization which provides enhanced cohesion due to Coulombic interaction between two neighbouring hard segments and causes disruption of the order in the hard segments.

The emulsification of the PU ionomer solution can lead to a slight increase in phase mixing and decrease in the three tensile properties. During the emulsification, the water enters the hard domains in the following sequence: it first adsorbs on the surface of the hard-segment microionic lattices, then enters into the disordered hard

domains, and subsequently into the short-range and long-range ordered hard domains successively.

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