

Effect of Diisocyanate Structure on Viscoelastic, Thermal, Mechanical and Electrical Properties of Cast Polyurethanes

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Synopsis

Structure property relationship of four different diisocyanates is studied in detail. The isocyanates selected are TDI, MDI Crude, HDI, and IPDI. Physical properties such as mechanical, dynamic mechanical, electrical, and thermal are studied. Dynamic mechanical analyses are based on the compound resonance principle. Among all, IPDI-based polymer showed mediocre trend and TDI-based polymer showed best properties.

INTRODUCTION

Solid polyurethanes are now widely utilized as engineering materials in many industries and are well known for their outstanding mechanical properties.

Diisocyanates have profound effects on the properties of polyurethane.¹ Commonly used diisocyanates are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Use of TDI is hazardous and presents handling problems. In order to find a substitute for TDI, work has been undertaken to study various isocyanates with respect to structure. Four different isocyanates (aromatic, bulkier aromatic, cyclic, and aliphatic) were selected. Influence of structure on physical properties such as mechanical, dynamic mechanical, electrical, and thermal, are studied.

EXPERIMENTAL

Materials

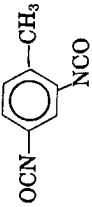

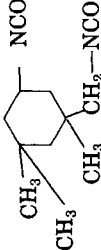
Chemicals used in the synthesis of polyurethanes are described in Table I. The diisocyanates were used as received and butanediol was distilled before use.

POLYURETHANE SYNTHESIS

Oxyester was demostured under reduced pressure before use. Polyester (1.0 mole) was reacted with diisocyanates (3.2 moles) viz. TDI, MDI (crude), HDI, and IPDI at 55 to 60°C. The mixture was stirred continuously for half

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TABLE I
Materials Used

Materials (designation)	Structure	Notes	Source
Base polyol Oxyester T 1136	Linear	Hydroxyl value = 105 Acid value = <2 colorless viscous liquid	CHEMISCHE Werke huls AG W. Germany
Diisocyanate 2,4-Toluene diisocyanate (TDI)		80% 2,4- + 20% 2,6- isomeric mixture	FLUKA AG Switzerland
Diphenyl methane diisocyanate (crude MDI)		Mixture of di- and tri- isocyanates Dark brown viscous liquid	EMERCK
1,6-Hexamethylene diisocyanate (HDI)	$\text{OCN}-(\text{CH}_2)_6-\text{NCO}$	—	AIDRICH England
Isophoron diisocyanate (IPDI)		NCO content 37.6% by wt purity >99.0% by wt	CHEMISCH W. Germany
Low-molecular weight diol 1,4-Butanediol (BD)	$\text{HO}-(\text{CH}_2)_4-\text{OH}$	—	BDH England
Catalyst Dibutyltinlaurate (DBTDL)	—	Used with IPDI	—

an hour to get a prepolymer with terminal NCO groups. The prepolymer was further reacted with butanediol (2.0 moles) and mixture was stirred continuously for 15 minutes. The reaction mixture was degassed after becoming viscous and was poured on to a stainless steel die (coated with a silicon mold-releasing agent). The die was kept in an oven at 100°C for 24 h to obtain cured sheets, which were subjected to characterization after proper conditioning.

MEASUREMENTS

Mechanical properties—tensile properties, such as modulus at various elongations, tensile strength, elongation at break, were measured according to ASTM D-412 specifications. The properties were measured on a universal testing machine (Instron U.K.) with a cross-head speed of 500 mm/min. Dumb-bell shaped specimens were cut using a C-type die. Hardness measurements were carried out using a durometer. Abrasion loss was determined on a Zwick abrasion tester according to Din 53516 test.

Dynamic mechanical analysis (DMA) measurements were carried out on DuPont's DMA 982 model coupled with 1090 microprocessor-based thermal analyser. The instrument works on the principle of compound resonance. The resonance oscillation frequency is related to the elongation storage modulus, E' of the sample, while the extra energy needed to keep the system oscillating with a constant amplitude is a measure of damping. All samples in the present investigation were clamped vertically between two arms, giving a flexural mode of oscillations. Measurements were done from -80 to $+40^\circ\text{C}$ with a heating rate of $5^\circ\text{C}/\text{min}$ in nitrogen atmosphere with a 2.5 L/min purge rate of N_2 gas. The sample oscillation frequency and the damping signal in millivolts as a function of temperature were recorded on a floppy disc. The plots of $\text{Tan } \delta$ and \log tensile storage, E' against temperature were directly obtained using the standard program of the microprocessor.

Thermomechanical analysis (TMA) was carried out to detect glass transition temperature (T_g) of the elastomers. The samples were sufficiently cooled down using liquid nitrogen and heated with a uniform rate of $8^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on DT-30 (Shimadzu Corp., Japan). The plots of ΔT and % weight loss versus temperature were recorded simultaneously with a heating rate of $5^\circ\text{C}/\text{min}$ in oxidative atmosphere. Temperature scanned was from ambient to 500°C .

The volume and surface resistivity was measured on high resistance meter (Hewlett Packard 4329 A) and resistivity cell (HP 16008 A). The measurements were carried out at 27°C .

X-ray diffraction spectra (intensity versus angle 2θ) were obtained on diffractometer (Philips PW 1140). The scanning rate was $2^\circ/\text{min}$, from 4 to 30° and the transition was $\text{CuK}\alpha$.

RESULTS AND DISCUSSION

The equivalent stoichiometric amounts of the various diisocyanates were used in each experiment to enable us to draw conclusions about the effect of molecular structure on properties. The polymers prepared from TDI, MDI,

and IPDI were mostly clear, or transparent, but polymer prepared from HDI was hard and opaque. The change in hardness and opacity was considered to be due to crystallization of the hard urethane segments.

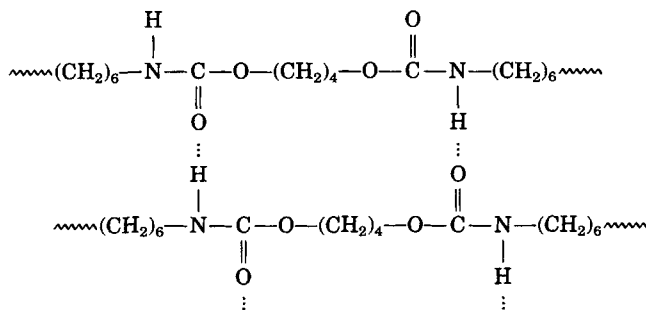
MECHANICAL PROPERTIES

Tensile strength, modulus, hardness, and abrasion loss were calculated and are given in Table II. Figure 1 shows the tensile behavior of various polyurethanes formed by different diisocyanates. The crude MDI-based PU showed least elongation and the slope of stress vs. elongation is maximum. The crude MDI is a mixture of di- and tri-isocyanates (55% 4,4'- and 2,4'-diphenyl methane diisocyanate, 25% triisocyanate, 20% polymeric isocyanate).^{2,3} Because of the higher functionality, a high degree of crosslinking takes place, consequently drastically reducing the elongation and imparting high modulus and hardness.

TDI-based PU seemed to show the best properties. This is due to following reasons. First, a higher rigidity imparted by direct association of isocyanate group with phenyl ring. Second, the higher reactivity of TDI which results from delocalization of negative charge on $-NCO$ by aromatic structure.

IPDI,* which has a cyclic structure, showed inferior properties when compared with TDI-based PU because of lack of delocalization of the negative charge on NCO, thereby reducing the reactivity of IPDI. The rigidity in IPDI is moderate because all cyclic carbon atoms are SP^3 hybridized and they maintain a nonplanar structure (chair configuration). The substituents on the cyclohexane ring reduce the symmetry and cause a general decrease in tensile and hardness properties.

HDI-based PU showed higher modulus properties (100%, 200%) compared to IPDI and even TDI, however, the tensile strength was substantially low compared to the former. The higher moduli values are due to presence of hydrogen bonding between two polymeric chains. This is facilitated by the even number of methylene groups present in diisocyanate as well as in the chain extender. (See the following figure)



The methylene sequence of HDI together with that of butanediol forms a tight crystalline structure, hence it shows higher moduli and hardness val-

* IPDI polymer without catalyst has shown very poor tensile properties because of its low reactivity. Therefore, we have used DBTDL catalyst in the case of IPDI polyurethane and properties of this PU are studied in detail.

TABLE II
Mechanical Properties of Polyurethanes (Oxyester/Disocyanate/BD System)

Diisocyanate	Modulus MPa			Tensile strength MPa	Elongation at break (%)	Hardness shore A	Abrasion loss	Density g/cc
	100%	200%	300%					
TDI	2.2	3.3	4.6	32.6	900	65	247	1.240
MDI crude	11.8	—	—	20	195	85	322	1.213
HDI	8.8	9.6	10.5	17	800	95	161	1.163
IPDI	3.6	4.7	6.2	24	900	58	259	1.160

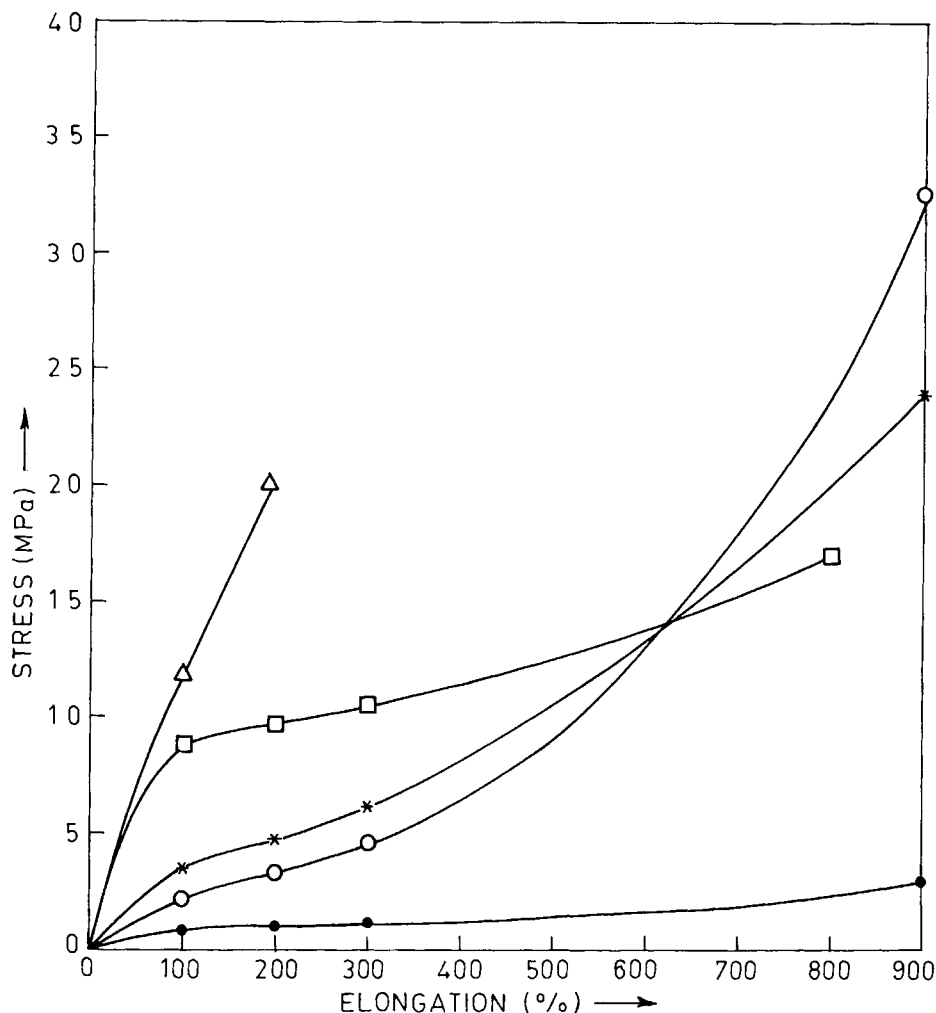


Fig. 1. Tensile behavior of (oxyester/diisocyanate/BD system) ○—TDI; △—MDI; □—HDI; ●—IPDI; *—IPDI (DBTDL).

ues. The low tensile strength of HDI polyurethane is due to lack of rigidity in the backbone chain.

DYNAMIC MECHANICAL PROPERTIES

The dynamic properties are shown graphically in Figures 2 and 3. Figure 2 shows the $\tan \delta$ values of each polymer as a function of temperature. The temperature at which $\tan \delta$ attains maximum, is determined as glass transition temperature (T_g).⁴⁻⁷ T_g of MDI-based PU is the highest and that of HDI based is lowest.

IPDI and TDI polyurethanes showed T_g close to each other. TDI PU showed higher T_g because of higher rigidity compared to that imparted by IPDI. Crude MDI, since it is polyfunctional, causes crosslinking, thereby increasing T_g however, compared to TDI and IPDI polyurethanes the increase is

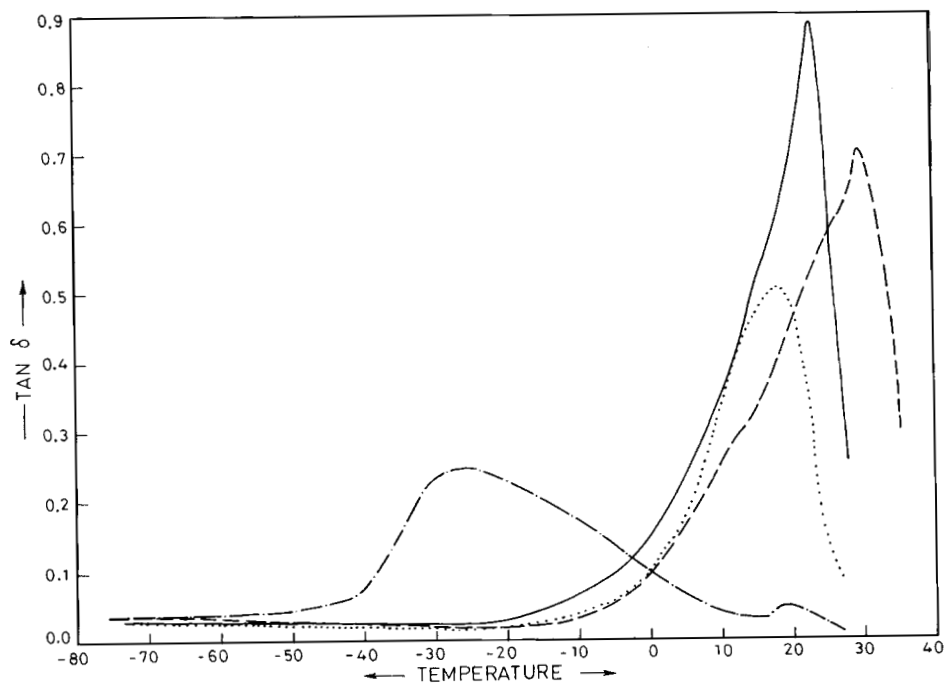


Fig. 2. $\tan \delta$ as a function of temperature (oxyester/diisocyanate/BD system) — TDI; --- MDI; -·- HDI; ··· IPDI.

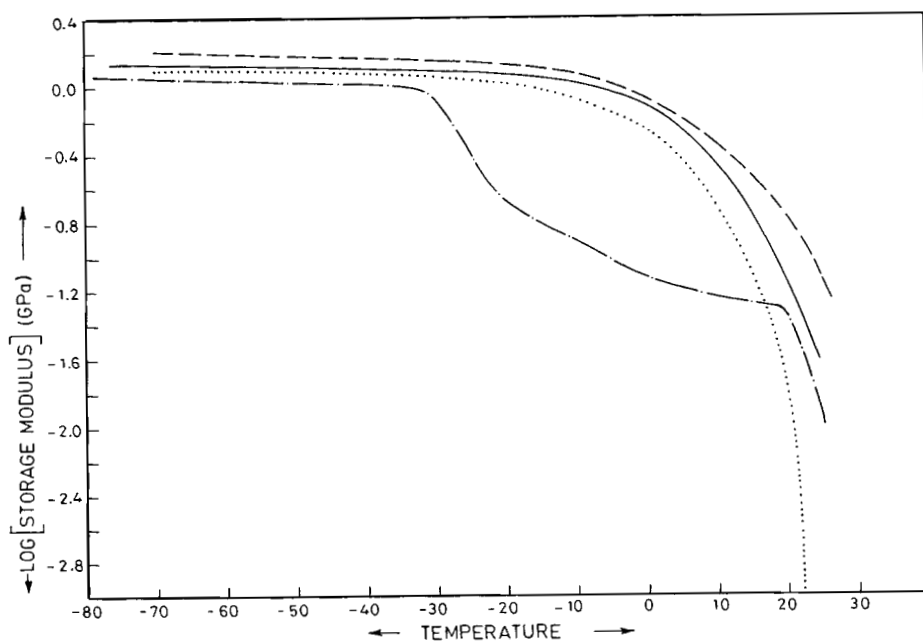


Fig. 3. Logarithm of storage modulus (GPa) as a function of temperature (oxyester/diisocyanate/BD system) — TDI; --- MDI; -·- HDI; ··· IPDI.

not substantial. This can be explained on the basis of $-\text{CH}_2-$ group in MDI which imparts flexibility and thereby lowers T_g . The net effects of the two factors is to increase T_g by a few degrees.

IPDI offers no crosslinking and imparts higher flexibility. Therefore it showed lower T_g among the three (TDI, MDI, IPDI) isocyanates. The lowest T_g shown by HDI is obviously due to maximum flexibility imparted by methylene sequences. The value for T_g obtained by DMA is approximately 30° higher than the value obtained from TMA.⁸ Considering the magnitudes of loss factor $\tan \delta$, IPDI polyurethane, which shows moderate value of $\tan \delta$ at working temperature, can be a good choice to increase durability of vibration mounts. HDI will be a totally wrong choice at this temperatures.

Storage modulus as a function of temperature is shown in Figure 3. Initially there is a marginal decrease in modulus, later as temperature increases a sudden fall of modulus occurs (inflection point). The inflection point corresponds to maximum in $\tan \delta$ vs. temperature graph.

The order of magnitude of storage modulus from -80 to $+15^\circ\text{C}$ is MDI $>$ TDI $>$ IPDI $>$ HDI. Thereafter, the order changes, at 20°C HDI shows higher modulus than IPDI. The above findings can be explained on the basis of crystallinity of HDI polyurethane. HDI PU showed two inflection points, one due to glass transition and the other due to melting of the crystallites. This type of behavior is also observed in other crystalline polymers.

THERMAL PROPERTIES

The detail thermal analysis of polyurethanes are given in Table III. Integral procedural decomposition temperature (IPDT) as proposed by Doyle⁹ provides a semiquantitative means for comparison of relative stabilities of various polymers. The MDI polymer shows highest IPDT values while HDI polymer shows lowest. The glass transition temperature determined on TMA is lowest for HDI polymer and highest for MDI polymer. The highest values of IPDT and T_g in the case of crude MDI polymer is due to high degree of crosslinking.

Two exotherms were observed in DTA thermograms. The values are shown in Table III. The crude MDI polymer is more thermally stable than any other polymer. HDI polymer shows the lowest decomposition temperature, indicating lowest thermal stability among the four isocyanates.

ELECTRICAL PROPERTIES

The volume and surface resistivity of these polymers are reported in Table IV. Almost all polymers show similar electrical resistivity. The affect of isocyanate structure is insignificant.

X-ray diffraction spectra obtained are shown in Figure 4. The spectra consisted of one broad halo¹⁰ in the region between $2\theta = 10$ to 28° for all polymers. HDI polymer has shown two sharp peaks at $2\theta = 22^\circ$ and 24° . This supports higher crystallinity in HDI polymer than any other polymer.

CONCLUSION

Four different isocyanates were selected to study structure property relationship. The high tensile properties, low elongation, and high thermal

TABLE III
Thermal Properties of Polyurethanes (Oxyester/Diisocyanate/BD System)

Diisocyanate	IDT °C	IPDT °C	Temp. at wt loss			Residue at 500°C (%)	Glass transition temp. on TMA (T_g) °C	Decomposition temperature on DTA	
			10%	30%	50%			1st °C	2nd °C
TDI	240	382	315	345	370	6	-8	310	415
MDI (crude)	270	411	315	370	410	24	-2	310	470
HDI	220	354	295	330	345	1	-50	290	315
IPDI	215	372	300	330	365	5	-18	315	405

TABLE IV
Surface and Volume Resistivity of Polyurethanes
(Oxyester/Diisocyanate/BD System)

Diisocyanate	Surface resistivity Ω	Volume resistivity Ω cm
TDI	1.5×10^{12}	5.6×10^{12}
MDI (crude)	1.8×10^{12}	6.9×10^{11}
HDI	1.6×10^{12}	1.8×10^{11}
IPDI	5.5×10^{11}	6.3×10^{11}

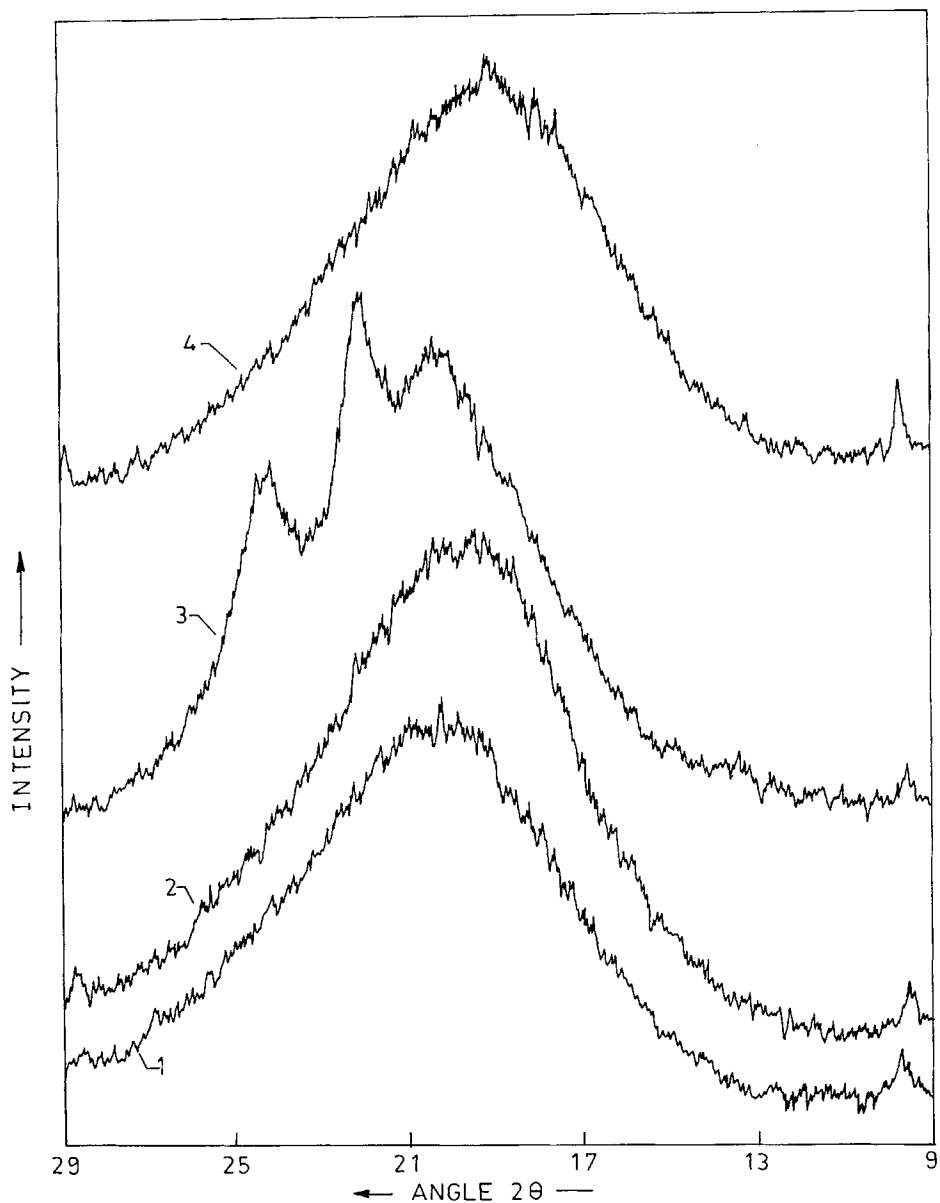


Fig. 4. Effect of diisocyanate on diffraction intensity.

stability, of MDI polymer are attributed to the formation of three-dimensional network. HDI polymer showed higher values of modulus but lower values of tensile strength, and higher values of storage modulus with two inflection points indicated crystalline nature. This was confirmed by X-ray diffraction spectra. Because of the crystallinity the applicability is restricted. IPDI-based PU showed mediocre trend. Among all, TDI-based PU showed best properties.

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