Chain-Extended Polyurethanes—Synthesis and Characterization

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ABSTRACT: Chain-extended polyurethanes (PUs) were prepared using castor oil and different diisocyanates such as toluene-2,4-diisocyanate and 4,4′-methylene bis(phenylisocyanate) as a crosslinker and different aromatic diamines like 4,4′-diaminodiphenyl methane and 4,4′-diaminodiphenyl sulphone as chain extenders. The effect of aromatic diamines on the swelling and thermal degradation behavior of PU have been discussed. A thermogravimetric analyzer (TGA) curve shows that all the chain-extended PUs are stable up to 194°C and that maximum weight loss occurs at 490°C. The TGA thermograms show that the thermal degradation of the PUs was found to proceed in two steps. The average molecular weight between crosslinks ($\bar{M}_c$) was determined by swelling studies. The properties imparted by the aromatic chain extenders are explained on the basis of groups present in the diamines. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 359–369, 2002; DOI 10.1002/app.10347

Key words: polyurethane; macrodiol; chain extenders; molecular weight; crosslinks; thermal stability

INTRODUCTION

Chain-extended polyurethane (PU) elastomers have a wide range of industrial applications, and they are well known for their mechanical properties. The three main ingredients of these elastomers are a long-chain polyol, a diisocyanate, and a chain-extender such as diamine. These polymers typically exhibit a two-phase morphology because of the incompatibility of the soft and hard segments. The excellent mechanical properties of PUs, such as high tensile strength and toughness, are primarily a result of the two-phase microstructure resulting from this phase separa-

tion.[1–4] The structure and the molecular weight of the macrodiol significantly influence the phase separation behavior and, consequently, the properties of the PUs. Previous studies[1–6] on structure–property relationships of PU were focused on polyether, polyester, and polycarbonate (PC) macrodiols. There has been some recent interest on PUs based on chain extenders such as diamines,[7] diols,[7] phenolphthalein,[8] and PDMS.[9]

A detailed literature survey reveals that the diamine chain-extended PU systems have not been studied thoroughly on transport and swelling characteristics. In view of the importance of PU membrane as a barrier material in several engineering areas,[10–11] it is important to know its swelling behavior with respect to common organic solvents. In continuation of our previous research,[12] in this article we report the swelling behavior, thermal properties, and morphology of aromatic diamine chain-extended PUs.

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Table I   Some Physical Properties of Solvents Used as Penetrants at 25°C

Penetrants	Molecular Volume (cm^3/mol)	Density (g/cc)	Solvent Parameter (cal cm^{-3})$^{1/2}$	ε
n-pentane	115.2	0.625	7.10	1.84
n-hexane	131.6	0.660	7.27	1.88
n-octane	163.5	0.704	7.57	1.95

EXPERIMENTAL

Materials

Castor oil (CO) was procured from the local market. Its molecular weight ($\bar{M}_n$) is 930 and its hydroxyl group/molecule[13] is 2.24. Toluene-2,4-diisocyanate (TDI), 4,4′-methylene bis(phenylisocyanate) (MDI), dibutyl tin dilaurate (DBTL), 4,4′-diaminodiphenyl methane (DDM), and 4,4′-diaminodiphenyl sulphone (DDS) were obtained from Sigma (USA), and were used as received. The organic solvents such as methyl ethyl ketone (MEK), n-pentane, n-hexane, and n-octane of AR grade were distilled before use. Some physical properties of solvents used as penetrants are shown in Table I. The polymer samples were cut circularly (diameter = 1.5 cm) using a sharp-edged steel die. The thickness of the specimens were made at several points and ranged from 0.35 to 0.50 cm (precision ±0.001 cm). The cut PU specimens were dried in a desiccator for two days before the experiment. Dry weights of the cut samples were taken before immersion into the airtight, metal-capped test bottles containing the penetrant. After immersion into the respective liquids, the bottles were placed in a thermostatically controlled oven (±0.5°C).

Synthesis of Chain-Extended Polyurethanes

Castor oil (0.001 mol) was dissolved in 50 mL of MEK in a 250-mL round bottom flask. This was reacted with diisocyanate (0.0022 mol) using two to three drops of DBTL as a catalyst. The contents of the flask were stirred mechanically for about 1 h at 60–70°C. The prepolymer so obtained was reacted with the equal molar ratio (0.001 mol) of diamine dissolved in MEK. The mixture was stirred for about 20 min at the same temperature. Then the mixture was poured into glass molds and left to dry at room temperature (25°C). The

film thus formed was cooled slowly and was removed from the mold. In the same way, different PUs were prepared using different diisocyanates and diamines.

Techniques

The density, surface hardness, and water vapor transmission rate (WVTR) were measured as per ASTM D792-86, ASTM D785, and ASTM D-96, respectively. Fourier transform infrared (FTIR) spectroscopy spectra were recorded using a Bruker IFS-25 FTIR instrument (USA). The IR spectra were recorded for the thin film of chain-extended PU. The IR spectrum was recorded in the wave number range of 4000–400 cm^{-1}.

Dynamic Swelling Studies

In each experiment, two preweighed, initially dry films were placed in solvents as per the requirement. Periodically, these samples were removed from the solution and weighed after removing the excess solvent from the surface using tissue paper. The same procedure was repeated at different time intervals. The swelling capacity of these films were determined as per the following equation:

grams of solvent per gram of polymer samples

$$= \frac{\text{swollen weight} - \text{dry weight}}{\text{dry weight}}. \quad (1)$$

The penetration velocity (ν) of solvents in each polymer was determined by the weight gain method as described by Peppas and coworkers.[14,15] The penetration velocity was calculated from the slope of the initial portion of the penetrant uptake curve by using the equation

$$\nu = \frac{1}{2\rho A^*} \frac{dwg}{dt}, \quad (2)$$

where dwg/dt denotes the slope of the weight gain versus time curve, and ρ is the density of solvent at 25°C. A^* is the area of the one face of the film, and the factor 2 accounts for the fact that penetration takes place through both sides.

The mass uptake of the swelling solution M_t as a function of time t was analyzed according to the equation[16]
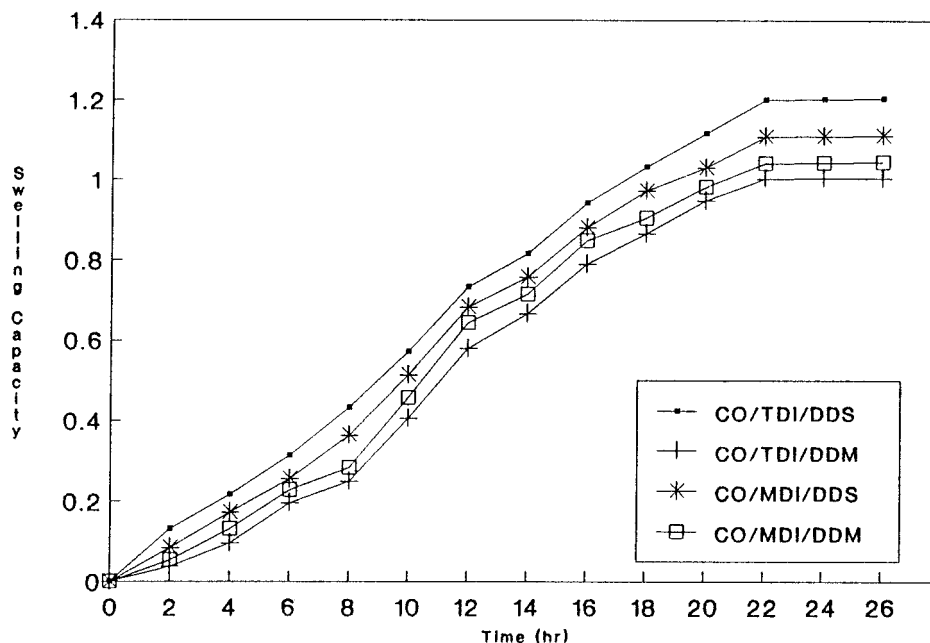
Figure 1 Swelling capacity versus time for all chain-extended polyurethanes in n-pentane at 40°C.

$$(M_t/M_\infty) = Kt^n, \tag{3}$$

which could be used to find out the Fickian and non-Fickian release behavior. M_∞ is the mass uptake of solvent at equilibrium, K is a constant related to the characteristics of the macromolecular matrix, and n is the exponent describing the Fickian or anomalous swelling mechanism. Using the natural logarithm of equation (3),

$$\ln(M_t/M_\infty) = n\ln(t) + \ln(K); \tag{4}$$

n and K can be calculated from the plot of $\ln(M_t/M_\infty)$ against $\ln(t)$.

The diffusion coefficient (D) can be calculated[17,18] as

$$D = \pi[h\,\theta/4M_\infty]^2, \tag{5}$$

where θ is the slope of the linear portion of the curve (Figs. 1–4); h is the thickness of the sample; and M_∞ is the maximum mass uptake, which has been estimated by the least-square procedure. However, an approximation was made here by considering the slight sigmoidal shape as a linear one.

The average molecular weight between cross links ($\bar{M}_c$) and the amount of network chain per unit volume were calculated from swelling studies using the relation developed by Flory-Rehner[19]:

$$\bar{M}_c = \frac{\rho_p V \phi^{1/3}}{[\ln(1-\phi) + \phi + x\phi^2]} \tag{6}$$

The thermal stability of the samples was assessed using a DuPont 2000 TA (USA) with 951 TGA instrument. The TGA scans were taken over a temperature range of 30–800°C, at a heating rate of 10°C/min in nitrogen atmosphere.

The surface morphology was studied using a scanning electron micrograph (SEM). The micrographs of the PUs were taken on SX-50 with probe microanalysis Sl. 320 after gold (100A°) coating. The planar view of the PU samples were scanned. The magnification is displayed on the respective microphotographs of the samples.

RESULTS AND DISCUSSION

The physical properties such as density and WVTR of chain-extended PUs were given in Table II. The density for all the chain-extended PUs lies in the range of 1.06–1.15 g/cc, and is within the
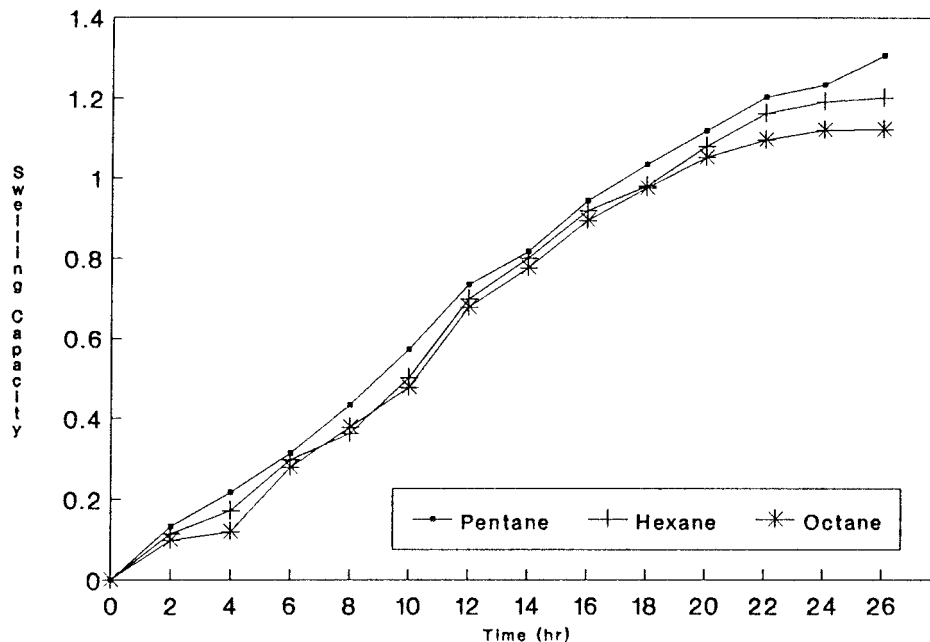
Figure 2 Swelling capacity versus time for castor oil/4,4′-methylene bis(phenyl iso-cyanate)/4,4′-diaminodiphenyl methane with different n-alkanes at 40°C.

expected range. Permeability to WVTR is of utmost importance in deciding the protective properties of PU membranes in packaging industries.

It was observed that the WVTR value for chain-extended PUs lies in the range of 38–46 g/m^2 per 24 h at 38°C/90% RH.
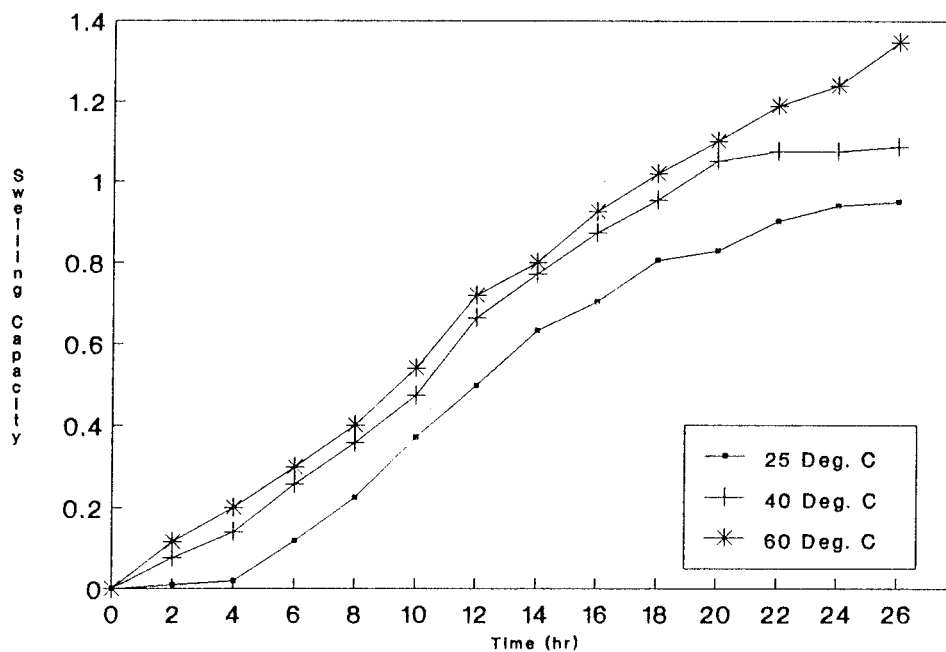
Figure 3 Swelling capacity versus time for castor oil/4,4′-methylene bis(phenyl iso-cyanate)/4,4′-diaminodiphenyl methane in n-pentane at different temperatures.
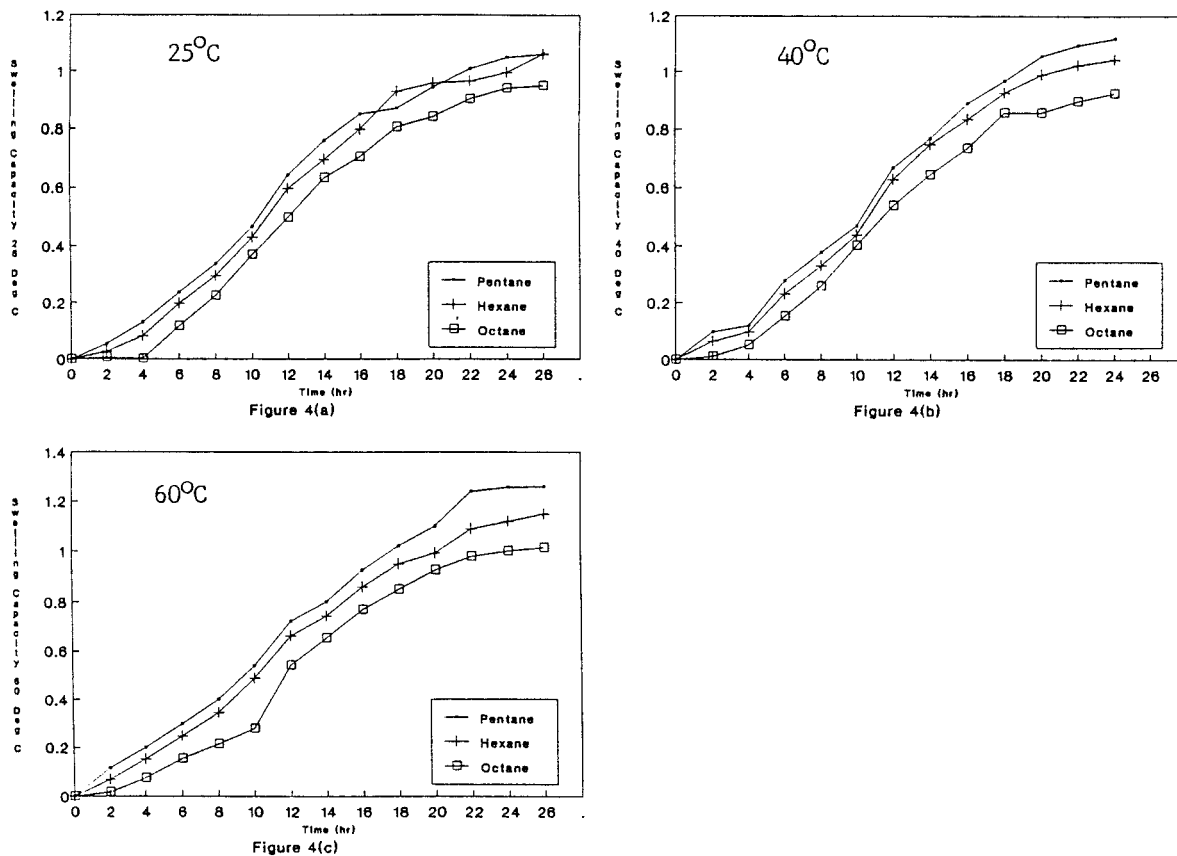
Figure 4 Effect of temperature on swelling behaviour of castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl methane in n-alkanes.

FTIR Spectra

The FTIR results of PUs are in accord with the expected structure. The broad peak at 3400–3200 cm^{-1} is the N–H stretching of the urethane linkage with finite contribution from extensive hydrogen bonding of the system.[20] We observed a peak in the range of 3100–3180 cm^{-1}, which is caused by aromatic C–H. The presence of the peak at 1760 cm^{-1} is because of carbonyl link of urethane.

A peak in the range of 1570–1600 cm^{-1} is because of the aromatic ring.

Swelling Studies

This investigation describes the effect of two aromatic diamines such as DDS and DDM on swelling behavior in n-aliphatic hydrocarbon solvents like n-pentane, n-hexane, and n-octane (Tables

Table II Physico-Chemical Properties of Aromatic Diamine Chain-Extended PUs

Samples	Density (g/cc)	WVTR (g/m² per 24 h at 38°C/90% RH)	Surface Hardness (Shore A) ± 3
CO + TDI + DDS	1.15	40	85
CO + TDI + DDM	1.12	38	81
CO + MDI + DDS	1.09	42	91
CO + MDI + DDM	1.06	46	89

CO = castor oil, TDI = toluene-2,4-diisocyanate, DDS = 4,4′-diaminodiphenyl sulphone, DDM = 4,4′-diaminodiphenyl methane, MDI = 4,4′-methylene bis(phenyl isocyanate), Shore A = unit of surface hardness.

Table III Swelling Analysis of Chain-Extended Polyurethanes in n-Pentane over a Period of 26 Hours

Temperature and System	Swelling Capacity (g solvent/g polymer)	Penetration Velocity ($\nu \times 10^5$ cm/s)	n	K	Diffusion Coefficient ($D \times 10^6$ cm^2/s)
25°C:					
A	1.18	0.30	0.64	0.20	2.32
B	1.10	0.38	0.63	0.19	3.43
C	1.01	0.39	0.56	0.22	2.71
D	1.00	0.45	0.62	0.26	2.27
40°C:					
A	1.25	0.30	0.62	0.22	3.06
B	1.14	0.47	0.57	0.20	3.62
C	1.06	0.47	0.55	0.23	2.80
D	1.01	0.55	0.53	0.29	2.32
60°C:					
A	1.27	0.60	0.60	0.30	3.85
B	1.19	0.82	0.56	0.32	3.65
C	1.07	0.83	0.54	0.29	2.92
D	1.01	0.96	0.52	0.31	2.50

A = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl sulphone; B = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl methane; C = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl sulphone; D = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl methane.

III and IV). The influence of the nature of the solvent on sorption kinetics of different chain-extended PUs in n-pentane at 40°C is shown in Figure 1.[21,22] The sorption kinetics are markedly influenced by the structure of crosslinkers and chain extenders. From Figure 1 it was observed

Table IV Swelling Analysis of Chain-Extended Polyurethanes in n-Hexane over a Period of 26 Hours

Temperature and System	Swelling Capacity (g solvent/g polymer)	Penetration Velocity ($\nu \times 10^5$ cm/s)	n	K	Diffusion Coefficient ($D \times 10^6$ cm^2/s)
25°C:					
A	1.14	0.28	0.63	0.22	2.21
B	1.00	0.29	0.61	0.21	3.32
C	0.99	0.30	0.62	0.23	2.50
D	0.96	0.32	0.60	0.25	2.01
40°C:					
A	1.13	0.31	0.63	0.25	2.88
B	1.03	0.35	0.60	0.23	3.20
C	0.99	0.34	0.61	0.22	2.61
D	0.97	0.37	0.58	0.26	2.15
60°C:					
A	1.21	0.40	0.62	0.32	3.43
B	1.04	0.43	0.60	0.33	3.39
C	1.03	0.50	0.59	0.30	2.83
D	0.98	0.56	0.56	0.31	2.35

A = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl sulphone; B = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl methane; C = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl sulphone; D = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl methane.

Table V   Swelling Analysis of Chain-Extended Polyurethanes in n-Octane over a Period of 26 Hours

Temperature and System	Swelling Capacity (g solvent/g polymer)	Penetration Velocity ($\nu \times 10^5$ cm/s)	n	K	Diffusion Coefficient ($D \times 10^6$ cm²/s)
25°C:					
A	1.06	0.29	0.64	0.25	2.04
B	1.06	0.28	0.60	0.21	3.12
C	0.96	0.30	0.59	0.24	2.38
D	0.94	0.31	0.62	0.22	1.97
40°C:					
A	1.05	0.30	0.62	0.26	2.63
B	1.01	0.32	0.56	0.24	3.11
C	0.98	0.33	0.53	0.23	2.59
D	0.96	0.34	0.59	0.27	2.07
60°C:					
A	1.11	0.39	0.60	0.34	3.25
B	1.04	0.41	0.57	0.32	3.24
C	1.00	0.42	0.52	0.32	2.75
D	0.92	0.52	0.60	0.31	2.23

A = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl sulphone; B = castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl methane; C = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl sulphone; D = castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl methane.

that DDS chain-extended PUs show higher swelling behavior than DDM chain-extended PUs. Some typical plots at 40°C for CO/MDI/DDM with different n-alkanes are given in Figure 2. In pentane, the attainment of equilibrium was quicker than in the other penetrants. This may be because of the lower molecular volume of pentane penetrant.[21,22] The swelling capacity plots of the CO/MDI/DDM system with n-pentane are shown in Figure 3 at different temperatures. The swelling capacity of CO/MDI/DDM for different n-alkanes at 25°, 40°, and 60°C are shown in Figure 4(a)–(c), respectively. It is clear from these figures that as the temperature increases, the swelling capacity also increases.[21,23] The polymer matrix taken for swelling analysis is in the dry state initially, and when it comes in contact with a solvent it swells. As the temperature increases, the velocity of the swelling front also increases, leading to faster swelling as well as higher polymer relaxation.

The swelling capacity and penetration velocity for different n-alkane penetrants are shown in Tables III–V. Here, it is noticed that swelling capacity and penetration velocity decrease with an increase in the molecular volume of the penetrants.

The values of n and K have been obtained from the least-square analysis. The average uncer-

tainty in the estimation of n is around ±0.008. The n values vary between 0.52 and 0.64, suggesting that their transport behavior is near-Fickian type. The n values do not show any systematic variation with temperature, but the K value increases with temperature, suggesting an increase in segmental motion with the raise in temperature. Furthermore, it appears that K depends not only on structural characteristics of the polymer and penetrant but also on solvent–PU interactions.

The diffusion coefficients (D) have been calculated using Eq. (5). A triplicate evaluation of D from the curves gave us D values with an error of ±0.003 unit at 25°C, ±0.004 unit at 40°C, and ±0.005 unit at 60°C for all chain-extended PUs. The variation of D depends on the nature of the penetrant molecules in addition to the composition of the PU. The value of D increases with increase in temperature. In all cases it is found that diffusivity decreases with an increase in chain length of n-alkanes. The inverse dependence of D either on molar volume or on number of carbon atoms of n-alkanes proves the conjecture that larger molecules in a related series of liquids occupy free volumes, leading to hindered diffusivities through the polymer matrix.

The calculated average molecular weight between crosslinks[24] of chain-extended PUs is given

Table VI   Average Molecular Weight between Crosslinks ($\bar{M}_c$) in Diamine Chain-Extended Polyurethanes by Swelling Studies

|	Average Molecular Weight between Crosslinks ($\bar{M}_c$) in		
Samples	Pentane	Hexane	Octane
CO + TDI + DDS	1571	1798	1683
CO + TDI + DDM	2745	2856	3054
CO + MDI + DDS	1941	2015	2153
CO + MDI + DDM	1609	1654	1737

CO = castor oil, TDI = toluene-2,4-diisocyanate; DDS = 4,4′-diaminodiphenyl sulphone, DDM = 4,4′-diaminodiphenyl methane, MDI = 4,4′-methylene bis(phenyl isocyanate).

in Table VI. From Table VI it was observed that molecular weight between crosslinks depends on the reactivity of the −NH hydrogen. $\bar{M}_c$ calculated for the samples using different solvents gave more or less the same value. This confirms that $\bar{M}_c$ is constant for a particular polymer.

Thermal Behavior

The thermal stabilities of chain-extended PUs were evaluated by TGA. A sample TGA thermogram is presented in Figure 5 for all chain-extended PUs. From thermograms (Fig. 5) it was observed that the thermal degradation pattern is almost identical for all chain-extended PUs. A two-step thermal degradation was observed in the TGA thermogram in the temperature ranges of 215°–432°C and 388°–530°C (Table VII) for first and second step, respectively, for all the PU samples. The obtained characteristic transition temperatures like temperature of onset of decomposition (T_0), temperature of 10% weight loss (T_{10}), temperature of maximum weight loss (T_{max}), and half volatilization temperature (T_{50}) from TGA curves are given in Table VIII. The relative ther-
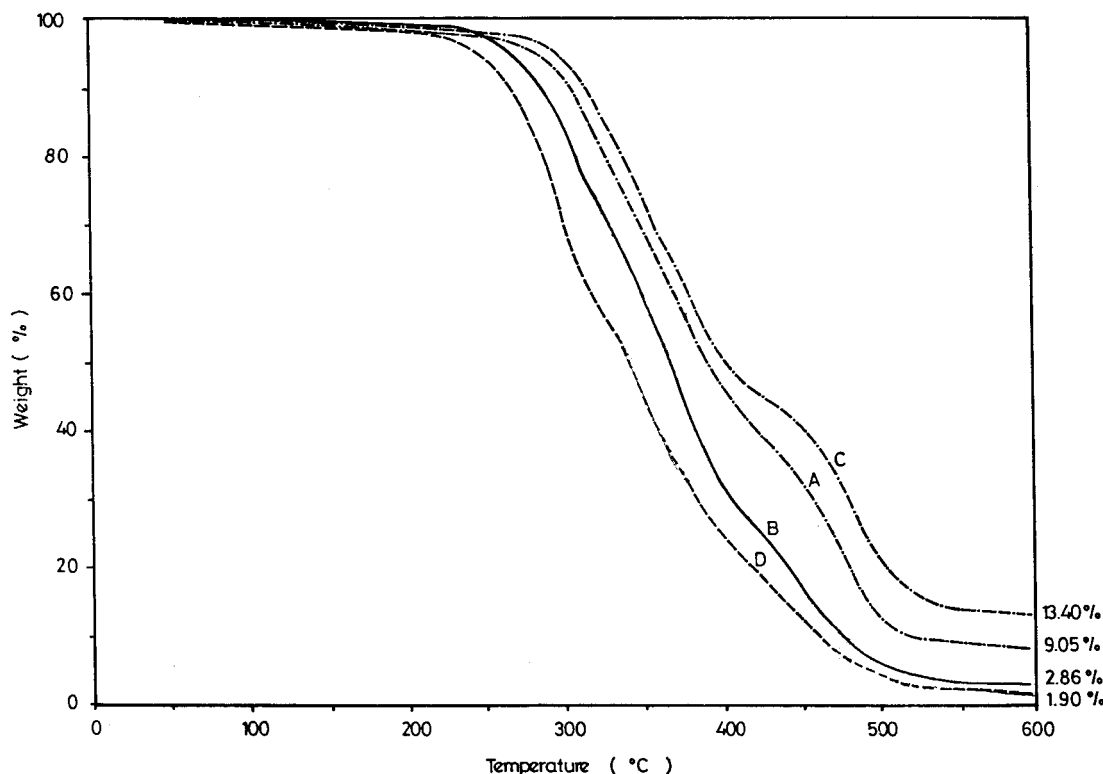
Figure 5   TGA thermograms of all chain extended polyurethane systems for (a) castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl sulphone; (b) castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl methane; (c) castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl sulphone; and (d) castor oil/4,4′-methylene bis(phenyl isocyanate)/4,4′-diaminodiphenyl methane.

Table VII Data Obtained from TGA Thermograms for Chain-Extended Polyurethanes

Samples and Process	Temperature Range (°C) ± 2	Weight Loss (%)
CO + MDI + DDS:		
1	230–409	73.0
2	409–490	24.1
Ash	· · ·	2.9
CO + MDI + DDM:		
1	270–388	72.0
2	388–493	26.1
Ash	· · ·	1.9
CO + TDI + DDS:		
1	230–431	80.0
2	431–530	6.6
Ash	· · ·	13.4
CO + TDI + DDM:		
1	215–432	63.0
2	432–510	28.0
Ash	· · ·	9.0

CO = castor oil, TDI = toluene-2,4-diisocyanate; DDS = 4,4′-diaminodiphenyl sulphone, DDM = 4,4′-diaminodiphenyl methane, MDI = 4,4′-methylene bis(phenyl isocyanate).

mal stabilities of the PUs were evaluated by comparing decomposition temperatures at various weight losses and integral procedural decomposition temperature (IPDT).[25] IPDT value represents the overall nature of the thermogram over the entire range of the TGA curves. The IPDT values of all the PUs lies in the range of 670°–710°C. From TGA thermogram it was observed that all the PUs were stable up to 194°C followed by rapid weight loss at 490°C. Complete decomposition was observed beyond 530°C. The temperature range of decomposition, the percentage weight loss and percentage ash content are given in Table VII for all chain-extended PUs. The first-step weight loss occurs in the temperature range of 215°–432°C with a weight loss of 63–80%, which represents the loss of base PU, oligomer, and moisture content. The second-step weight loss can be attributed to the complete decrosslinking of the chain-extended PU,[25,26] which occurs in the temperature range of 388°–530°C with a weight loss of 6.6–28%. The order of thermal stability observed from Table VII is CO/MDI/DDS > CO/TDI/DDS > CO/MDI/DDM > CO/TDI/DDM. This means that a higher stability was observed for the CO/MDI/DDS crosslinked system.

Scanning Electron Micrograph

The surface morphology of chain-extended PUs was studied by SEM. The electron micrographs of the surface of the PUs are shown in Figure 6(a–b) for CO/TDI/DDM and CO/TDI/DDS, respectively. From SEM photographs, spherullite structure was observed. This is a result of hard segment domains contributed by both aromatic chain extender and diisocyanate crosslinks to PU. Figure 6(b) shows two-phase morphology because chain-extended PUs consist of both hard and soft segments.

CONCLUSIONS

The work described here summarizes the results of swelling capacity, thermal stability, and morphology of structurally different aromatic diamines chain-extended PUs. It is observed that the

Table VIII Transition Temperature and IPDT Values Obtained from TGA for Diamine Chain-Extended Polyurethanes

Samples	Transition Temperature (°C) ± 2					IPDT (°C) ± 2
	T_0	T_{10}	T_{20}	T_{50}	T_{max}	
CO + TDI + DDS	196	300	315	370	490	710
CO + TDI + DDM	194	320	345	398	530	670
CO + MDI + DDS	198	315	342	394	510	725
CO + MDI + DDM	200	320	345	398	515	695

CO = castor oil, TDI = toluene-2,4-diisocyanate; DDS = 4,4′-diaminodiphenyl sulphone, DDM = 4,4′-diaminodiphenyl methane, MDI = 4,4′-methylene bis(phenyl isocyanate).
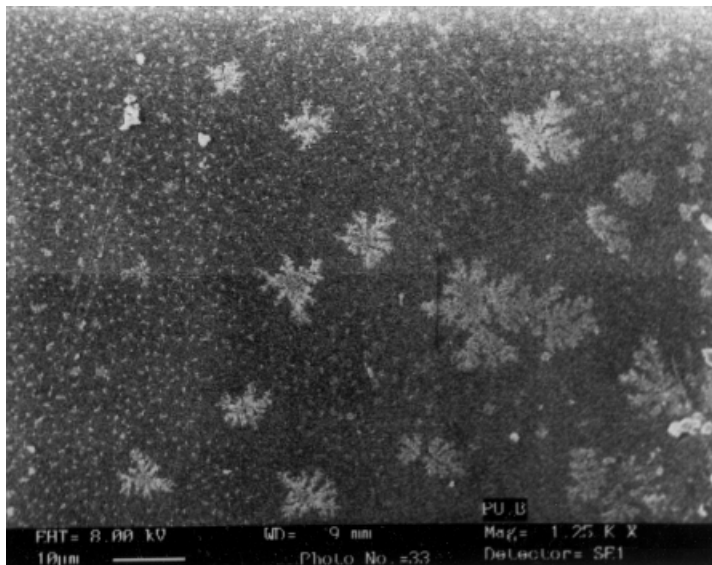
(a)
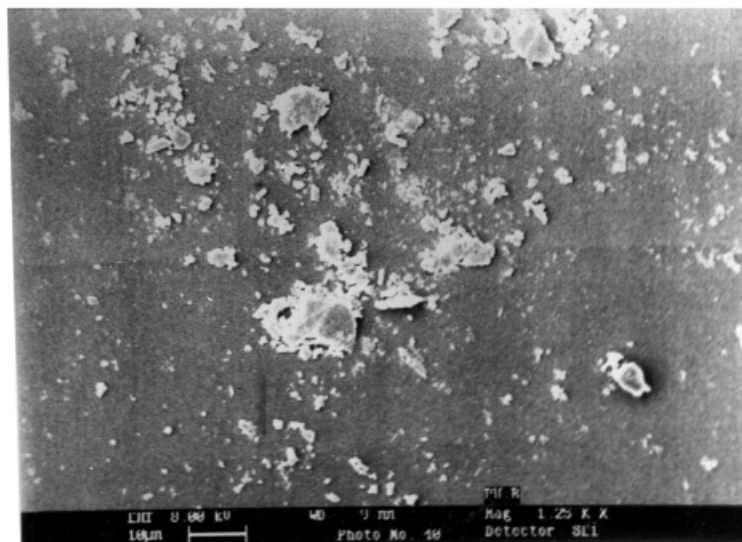
(b)

Figure 6 Scanning electron microscope photographs for (a) castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl methane and (b) castor oil/toluene-2,4-diisocyanate/4,4′-diaminodiphenyl sulphone.

size, viscosity, and solubility parameters of the solvent and the chemical nature of the chain-extended PUs seem to exert influence on the swelling capacity. All chain-extended PUs with pentane have higher swelling-capacity values, ranging from 1.18 to 1.258 g solvent/g polymer.

The TGA thermograms of chain-extended PUs show two-step thermal degradation behavior because of the complicated chemical structure of PUs. SEM photographs shows two-phase morphology.

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