Asian Journal of Chemistry; Vol. 29, No. 5 (2017), 951-959

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20327

Thermo-Mechanical Characteristics of Shape Memory Polyurethane Varying Molecular Weight of Polyol

SHAZIA NAHEED[1], MOHAMMAD ZUBER[1,*], MEHDI BARIKANI[2], IFTIKHAR HUSSAIN BUKHARI[1] and KHALID MAHMOOD ZIA[1]

[1]Institute of Chemistry, Government College University, Faisalabad-38030, Pakistan
[2]Iran Polymer and Petrochemical Institute, Tehran, Iran

*Corresponding author: Fax: +92 041 9200671; Tel: +92 321 6682375; E-mail: mohammadzuber@gmail.com

Received: 5 October 2016; *Accepted*: 13 January 2017; *Published online*: 10 March 2017; AJC-18280

A series of shape memory polyurethanes (SMPUs) have been prepared from polycaprolactone diol (PCL, $\bar{M}n$ 400, 750, 1000, 1250, 1600, 2000, 3000 and 4000 g mol^{-1}), 1,2-ethanediol (1,2-EDO) and 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI). The structural identification of final polymers was confirmed by FT-IR and NMR (^{1}H NMR, ^{13}C NMR) spectroscopy. The thermo-mechanical characteristics was studied using differential scanning calorimeter, thermo-gravimetric analysis, dynamic mechanical thermal analysis and shape memory test by tensile cyclic loading using temperature controlled chamber. The absence of any peak corresponding to functional groups (–OH, –NCO) of monomers in FT-IR spectra confirmed the completion of reaction. The DSC thermograms showed the gradual decrease in the thermal transition with increasing crystallinity, which has been confirmed by dynamic mechanical thermal analysis, with corresponding increase in the molecular weight of macrodiol used as soft segments. The shape recovery of the shape memory polyurethane went up to 90 % and retention up to 79 %. The polymer based on higher molecular weight of polycaprolactone diol (4000 g mol^{-1}) showed better shape memory behaviour than low molecular weight.

Keywords: Thermo-mechanical, Polyurethane, Polyol, Polycaprolactone diol.

INTRODUCTION

Polyurethanes are widely synthesized industrial material, which can be prepared by polyaddition reaction of diisocyante, polyol and chain extender [1,2]. Polyurethane has the ability to remember their shape called shape memory polyurethanes (SMPUs). The external stimulus like heat, light *etc.*, can convert temporary shape to original one and their applications have been expended steadily [3-5]. The thermoplastic polyurethane mostly consists of linear and multiblock copolymer that can be segregated into soft and hard segments. These segments are dependent on phase morphology [6]. Recently, the SMPUs have attained a vast concentration as functional material due to its lot of properties and applications. The types, composition and molecular weight of soft and hard segments are all accountable to design biocompatibility, shape recovery and shape retention of SMPUs. The molecular designed based SMPUs could be amorphous/crystalline showing the actuation temperature in wide range *i.e.*, -20 to 150 °C [7,8].

Shape memory polyurethanes are consisted of both chemical and physical bonding net work. The network of these polymers consist of different chain segments and net points. These networks are helpful to attain the structure recovery as well as permanent shape. The control of glass transition temperature (T_g) specially at room temperature is one of the best property of SMPUs among other SMPs [9-11].

Initially shape memory properties were obtained in alloys. The major advantage of SMPUs is their light weight and less cost as compared to shape memory alloys. The shape memory effect (SMEs) dependable on frozen (hard segment) and reversible (soft segment) phase [10]. The molar ratio of phases, polymerization methods and soft segment molecular weight, all can control the SMEs. The structural, thermo-mechanical and ionization behaviours of SMPUs have been broadly investigated [11,12]. The glass transition temperature of hard domains found to be high as compared to soft domains due to intermolecular interaction. Meanwhile, the soft segments endow typical feature including low modulus and high elastic recovery. The hard segments content can be improved either controlling molecular weight or mole ratio of soft segments. Moreover, both the polyol's type and chain exterder's structure found to be important factor that influenced the physical and phase separation properties of SMPUs [13]. A large number of series of SMPUs have been developed to date by using different polyol, chain extenders and aliphatic or aromatic diisocyanates [14-16].

However, there has been less research reported on the molecular structure and shape memory behaviour of SMPUs varying a range of molecular weight of polycaprolactone diol. Keeping in view these aspects an attempt has been made to show the clear picture of the thermo-mechanical characteristics of these polyurethanes. These successful outcomes of this project will make a valuable effort in the field of polymer engineering.

To understand the structural properties correlation based on different/varying chain length of soft segments of shape memory polyurethanes, a series of eight samples has been prepared. In this paper the thermo-mechanical properties of SMPUs and their structure verification were analyzed by TGA, DSC, DMTA, cyclic tensile test, FT-IR and NMR techniques, respectively.

EXPERIMENTAL

4,4′-Dicyclohexylmethane diisocyanate (H_{12}MDI) and 1,2-ethanediol (1,2-EDO) were supplied from Sigma-Aldrich Chemical Co. Polycaprolactone diol CAPA 2047A, CAPA 2077, CAPA 2100A, CAPA 2125A, CAPA 2161, CAPA 2200A, CAPA 2302A and CAPA 2403A (molecular weight 400, 750, 1000, 1250, 1600, 2000, 3000 and 4000 g mol^{-1}, respectively) were denoted by Perstorp Polyols (Solvay Chemicals), Inc. Toledo. Ohio. The PCL and 1,2-EDO were kept at 70 °C in vacuum oven for 24 h, to avoid the interference of water vapours or air bubble during reaction. Molecular weight of all the CAPA molecules were confirmed by applying the procedure reported in ASTM D-4274C [17], whereas H_{12}MDI was used as received.

Synthesis: Shape memory polyurethanes have been synthesized by following two step syntheses:

Synthesis of NCO terminated polyurethane prepolymer: The synthesis of SMPU was carried out according to already proposed method [18]. In first step polycaprolactone diol (0.8 mol) was mechanically stirred in four-necked round bottom flask equipped with condenser and nitrogen gas in-let. Polycaprolactone diol was stirred continuously at 60-70 °C for few minutes. Then 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI) (2 mol) was stirred at 100 °C. During optimization of the experimental conditions, it took 2 h for preparation of NCO terminated prepolymer (Fig. 1a). The preparation of prepolymer was confirmed by FTIR analysis (Fig. 2c).

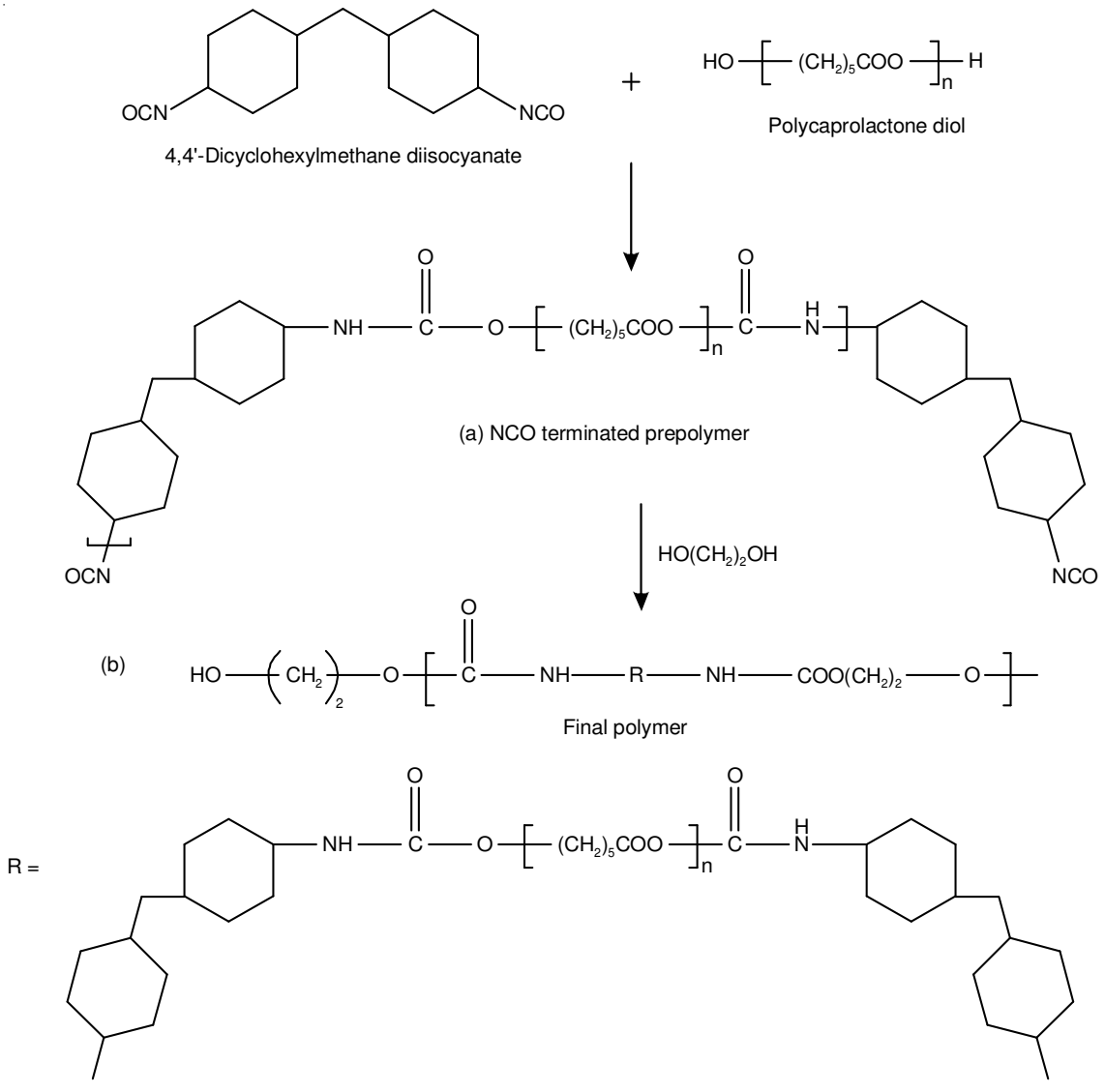

Fig. 1. Synthesis of shape memory polyurethane containing polycapro-lactone diol as soft segment (a) Step 1: Preparation of NCO terminated SMPU prepolymer (b) Step 2: Final proposed SMPU

Synthesis of shape memory polyurethane: After preparing the NCO (isocyanate) terminated prepolymer, a chain extender *i.e.*, 1,2-EDO (1.2 mol) was added into the reaction mixture and kept on stirring for further 30 min at 90 °C. A transparent, thick and viscous material was found in the flask, which indicated the formation of SMPU. The prepared sample was poured into a Teflon plate and placed the sample in vacuum oven at 100 °C and cured for 24 h [18]. The sample (cured) stored at ambient temperature; *i.e.*, 25 °C and relative humidity (Fig. 1b).

Following the above procedure, series of eight samples were prepared by varying the molecular weight of polycaprolactone diols. The mole ratio of all these samples is given in Table-1. The cured samples were saved for additional analysis. Figs. 1a-b representing chemical route for SMPU synthesis.

TABLE-1
THE SAMPLES CODES, RESPECTIVE MOLECULAR WEIGHTS OF PCL AND MOLAR RATIO OF THE REACTANTS IN SERIES OF MOLECULAR WEIGHT BASED SMPU SAMPLES

Samples code	PCL (MW) (g/mol)	Molar ratio of ($H_{12}MDI^b$/PCL[a]/EDO[c])
SMPU1	400	2:0.8:1.2
SMPU2	750	2:0.8:1.2
SMPU3	1000	2:0.8:1.2
SMPU4	1250	2:0.8:1.2
SMPU5	1600	2:0.8:1.2
SMPU6	2000	2:0.8:1.2
SMPU7	3000	2:0.8:1.2
SMPU8	4000	2:0.8:1.2

[a]Polycaprolactone diol (PCL); [b]4,4'-Dicyclohexylmethane diisocyanate ($H_{12}MDI$); [c]1,2-Ethanediol

Molecular characterization: Molecular structure of synthesized polyurethane samples having various molecular weights of polycaprolactone diol (PCL) was confirmed using Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. FT-IR scans of the prepared SMPU samples were obtained by Equinox 55 Fourier transform infrared (FT-IR) Bruker, Germany, equipped with ATR assembly and ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO)-d_6 solution using a Bruker Advance 400 MHz spectrometer.

Thermogravimetric analysis (TGA): In order to quantify the decomposition temperature of samples, thermo-gravimetric analysis (TGA) was conducted using a TGA/DSC 1, Mettler Toledo, Switzerland. The prepared sample sheets were put in vacuum oven to remove the moisture. The sheets were then cut into pieces, about 10-20 mg each and heated from 30 to 600 °C and thermo grams were recorded at a constant rate of 10 °C/min (Table-2).

Differential scanning calorimeter (DSC): The DSC (Mettler Toleto, Switzerland) used to determine transition including glass transition (T_g), melting (T_m), crystallizatiion (T_c), with their respective enthalpies under a nitrogen purge (50 mL/min). The polymers were made by encapsulating confirmed weighed (11 mg) in a sealed aluminum pan. The samples were heated to 250 °C at a rate of 10 °C/min), then cooled to -100 °C and held for 0.5 min at -100 °C and then second heating rate of 10 °C/min from –100 to 300 °C. The values mentioned in Table-3 represent the different transitions taken from cooling and heating scans. Thermal characteristics of various SMPU(s) have been discussed by varying the molecular weight of PCL.

TABLE-3
THERMAL TRANSITIONS AND CORRESPONDING ENTHALPIES OF SHAPE MEMORY POLYURETHANE BASED ON $H_{12}MDI$, PCL AND 1,2-EDO

Sample code	Thermal transition (°C) with corresponding enthalpy (J/g)		
	T_g (°C)	T_c.s (°C)	T_m.s (°C)
SMPU1	70.29 (0.20)	–	–
SMPU2	7.92 (0.168)	–	–
SMPU3	-11.46 (0.131)	–	–
SMPU4	-36.16 (0.190)	–	–
SMPU5	-38.41 (0.280)	–	–
SMPU6	-53.73 (0.131)	–	–
SMPU7	-55.69 (0.315)	-9.66 (27.89)	42.72 (-42.43)
SMPU8	-53.74 (0.350)	–	45.38 (-38.52)

T_g = Glass transition temperature; T_c.s = Srystallization temperature of soft segments; T_m.s = Melting temperature of soft segments

Dynamic mechanical thermal analysis (DMTA): Dynamic mechanical thermal analysis measurements of the prepared polymer samples with dimensions; *i.e.*, 10, 6.69, 0.81 mm, 1 Hz frequency, scanned from -150 to 200 °C at a rate of 10 °C min^{-1} were performed in tension mode (Netzsch DMA 242C, Germany). The curves of storage modulus and tangent delta were recorded as function of temperature.

Shape memory test: Tensile mechanical analysis were measured by INSTRON Model: 6025 United Kingdom, applying ASTM D638 under the condition of 15 mm gauge length, 0.93

TABLE-2
THERMAL STABILITY DATA OF THE SMPU SAMPLES

Sample code	PCL[a]/$H_{12}MDI^b$/EDO[c] (mole ratio)	Polyol (MW)	T_{onset} (°C)	T_5 (°C)	T_{10} (°C)	T_{20} (°C)	T_{50} (°C)	T_{max} (°C)
SMPU 1	0.8:2:1.2	400	231	291	306	322	348	591
SMPU 2	0.8:2:1.2	750	236	298	313	328	347	580
SMPU 3	0.8:2:1.2	1000	237	298	316	334	358	592
SMPU 4	0.8:2:1.2	1250	258	311	328	345	369	593
SMPU 5	0.8:2:1.2	1600	253	303	320	337	363	592
SMPU 6	0.8:2:1.2	2000	266	312	329	343	366	590
SMPU 7	0.8:2:1.2	3000	259	317	332	347	375	592
SMPU 8	0.8:2:1.2	4000	277	322	339	356	395	593

T_{onset} = Initial decomposition temperature; T_5 = Temperature of 5 % weight loss (from TGA); T_{10} = Temperature of 10 % weight loss (from TGA); T_{20} = Temperature of 20 % weight loss (from TGA); T_{50} = Temperature of 50 % weight loss (from TGA); T_{max} = Maximum decomposition temperature (from TGA); [a]Polycaprolactone diol (PCL); [b]4,4'-Dicyclohexylemethane diisocyanate ($H_{12}MDI$); [c]1,2-ethanediol (EDO)

mm thickness, 3 mm width, 5 mm/min crosshead speed and 100 N load cells. The temperature controlled instrument was used for measuring cyclic shape memory test. In temperature controlled chamber the specimen with a length L_o was drawn (100 %) to 2 L_o at 60 °C for 3 min and stayed at 60 °C for 5-6 min. After that the sample in the chamber was cooled to -50 °C with the help of liquid nitrogen for 10 min, the shrunk length (L_1) was measured after 20 min after releasing lower grip. Shape retention (%) and shape recovery (%) were calculated by eqns. 1 and 2, respectively. Three reading were calculated for each sample.

$$\text{Shape retention } (\%) = \frac{L_i - L_o}{L_o} \times 100 \quad (1)$$

$$\text{Shape recovery } (\%) = \frac{2L_o - L_2}{L_o} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

FT-IR study: The FT-IR spectra of monomers 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI), polycaprolactone diol (PCL), isocyanate (–NCO) terminated polyurethane prepolymer, 1,2-EDO chain extender and final SMPU were taken in the range of 4000-750 cm^{-1} and are presented in Fig. 2. The spectra of H_{12}MDI (Fig. 2a) showed a strong peak at 2266 cm^{-1} recognized the isocyanate (–NCO) group attached to 4,4′-dicyclohexylmethane diisocyanate. The FT-IR spectra of PCL (Fig. 2b) were assigned as: 3736 cm^{-1} (–OH) stretching vibration); 2945 cm^{-1} (asymmetric $–CH_2$ stretching); 2861 cm^{-1} (symmetric $–CH_2$ stretching); 1724 cm^{-1} (C=O stretching); 1295 cm^{-1} (C–O and C–C stretching in crystalline phase); 1240 cm^{-1} (asymmetric C–O–C stretching); 1178 cm^{-1} (symmetric C–O–C stretching); 1101 cm^{-1} (C–O and C–C stretching in the amorphous phase). Fig. 2c presented FT-IR spectrum of –NCO terminated polyurethane prepolymer. Moreover, the disappearance of –OH groups signals, reduced intensity of –NCO groups along with appearance of –NH signal at 3325 cm^{-1} suggesting the formation of polymer. The other observed peaks in the FT-IR spectrum of polyurethane prepolymer were assigned as: 2945 cm^{-1} (CH asymmetric stretching of $–CH_2$); 2854 cm^{-1} (CH symmetric stretching of $–CH_2$); 1726 cm^{-1} (–C=O stretching of PCL). To get the final SMPU 1,2-EDO was used as chain extender. The FT-IR spectra of 1,2-EDO showed (Fig. 2d) a broad peak of –OH stretching vibration at 3736 cm^{-1} indicated the purity of chain extender. The asymmetric and symmetric peaks of $–CH_2$ were also confirmed due to their appearance at their appropriate positions. The FT-IR spectrum of final SMPU is shown in Fig. 2e. The spectrum of final SMPU showed the appearance of –NH peak a3325 cm^{-1} and disappearance of –NCO peak at 2266 cm^{-1} confirmed the formation of shape memory polyurethane reaction. The FT-IR analysis supports the predesigned structure of synthesized polymer. The FT-IR spectra of all SMPUs (Fig. 3) showed –NH stretching vibration peaks at 3770-3328 cm^{-1}. The CH symmetric and asymmetric stretching vibrations of $–CH_2$ groups were observed at 2862-2850 cm^{-1} and 2935-2920 cm^{-1}, respectively. The other peaks were assigned as: 1726-1698 cm^{-1} (–C=O bond) susceptible to molecular interaction between SMPU chains [19]; 1524-1521 cm^{-1} (NH deformations); 1468-1448

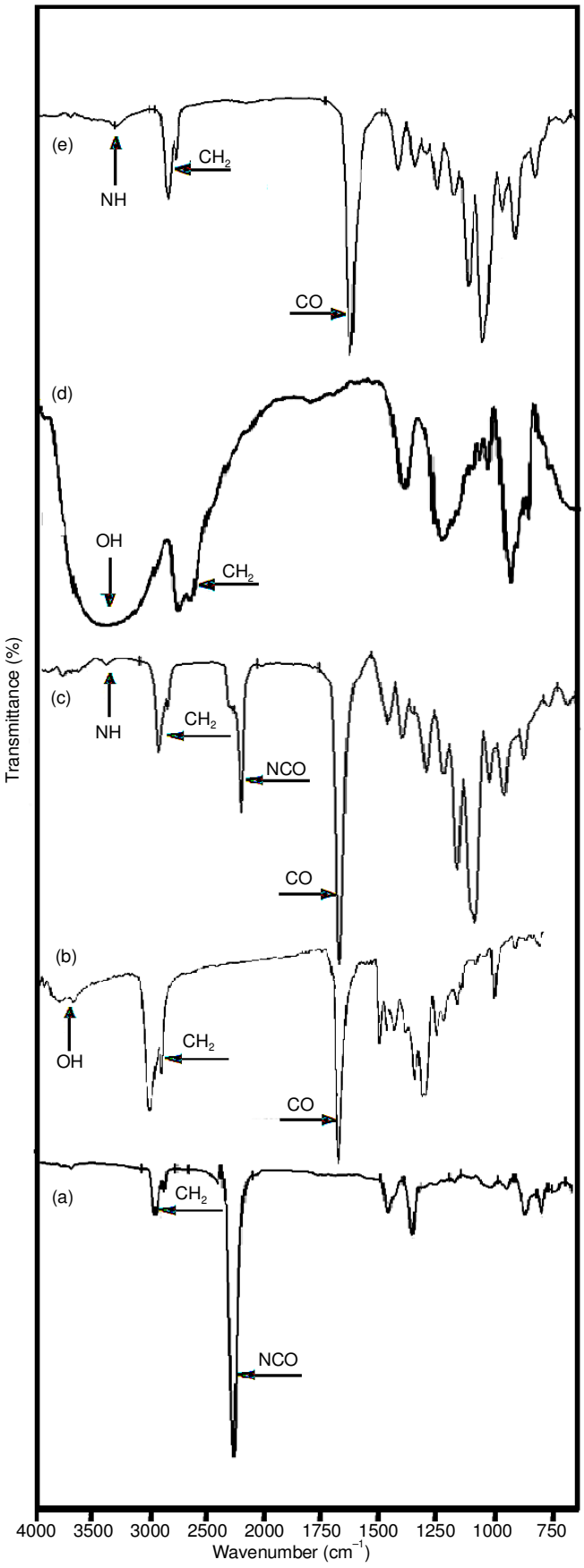

Fig. 2. FT-IR spectra: (a) 4,4′-dicyclohexylmethane diisocyanate (H_{12}MDI); (b) Polycaprolactone diol (PCL); (c) NCO terminated polyurethane prepolymer; (d) 1,2-ethanediol (1,2-EDO) and (e) Final shape memory polyurethane (SMPU)

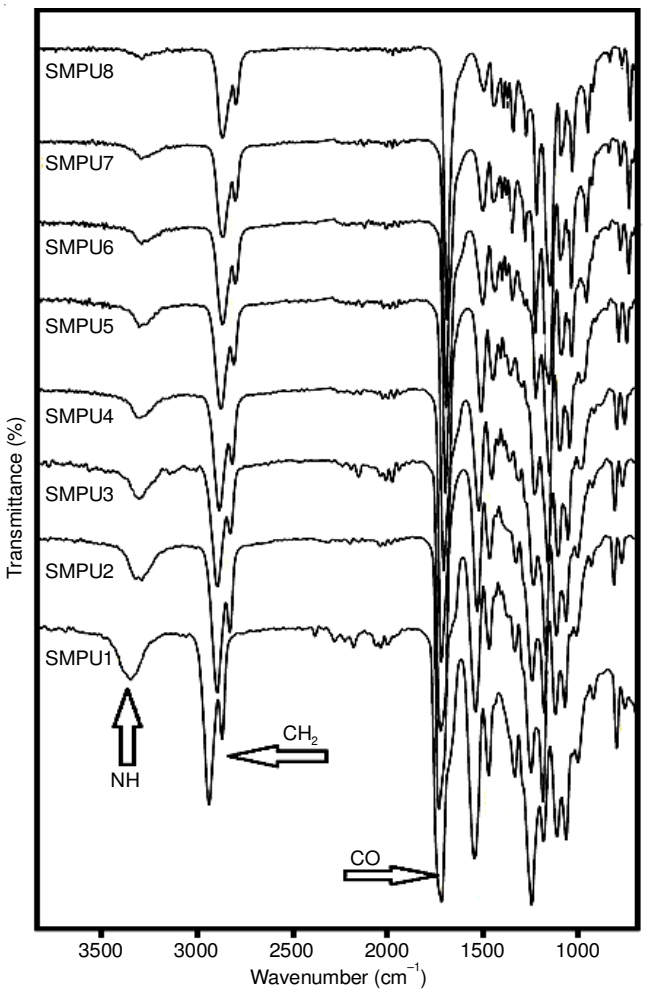

Fig. 3. FT-IR Spectra of SMPUs by varying molecular weight of PCL (bottom to top) SMPU1 (Mw: 400), SMPU2 (Mw: 750), SMPU3 (Mw: 1000), SMPU4 (Mw:1250), SMPU5 (Mw: 1600), SMPU6 (Mw: 2000), SMPU7 (Mw: 3000) and SMPU8 (Mw: 4000)

cm^{-1} (CH_2 bending vibration); 1412 cm^{-1} (CH bending vibration); 1306 cm^{-1} (CH_2 wagging). It was observed that the intensity of hydrogen bonded–NH increased with increasing molecular weight of PCL. Moreover, the –C=O peak of urethane groups shifted from 1698 to 1726 cm^{-1}, this shift is towards higher wave number indicated that polyurethane samples have PCL of high molecular weight has low tendency of H-bonding. This is also inferred from the sharpening of peaks. Sharpness of peaks was observed by increasing soft segment length. The results revealed that SMPU1 band showed maximum intermolecular hydrogen bonding at 1698 cm^{-1}. Usually, the stretching vibration of C=O group intermolecular interactions [18]. From FT-IR spectrum, it was thought that the increased length of soft segment had great affect on the morphological behaviour of SMPU.

Nuclear magnetic resonance spectroscopy (NMR): The molecular characteristic of the synthesized polymer samples were evaluated by ^{1}H NMR and ^{13}C NMR. The NMR spectra of polyurethane extended with 1,2-EDO (SMPU6), shown in Fig. 4 (a & b). Both ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (400 MHz, DMSO-d_6) spectra of final synthesized shape memory polyurethane (SMPU6) was in accordance with proposed structures. The ^{1}H NMR spectra shown in Fig. 4(a) presented the following peaks. The signal for urethane (–NH) was observed at 8.0 ppm (s, NH) and peaks observed at 1.27-1.78 ppm were assigned for non aromatic cyclic protons. The peaks appeared at 1.28-4.09 ppm, assigned for protons of $–CH_2OCO–$ and $–CH_2–$ supported the formation of polyurethane. The peaks assigned as: 8.0 ppm (s, NH); 3.78-3.30 (s, 2H); 4.41 (m, 2H); 2.47 (DMSO); 2.21 (m, 2H); 1.52-1.47 (m, 4H) and regarding ^{13}C NMR spectra in Fig. 4 (b); while the peaks assigned as; 173.1, 155.7 ppm (–C=O); 49.2, 34.0 ppm (cyclic CH); 31.5, 28.8 ppm (cyclic CH_2); 68.8, 64.2, 64.1, .63.9, 40.6, 40.4, 40.2, 40.0, 39.7, 39.5, 33.8, 28.6, 28.2, 25.7, 25.3, 24.6, 24.5, 21.7 ppm (CH_2).

Thermo-gravimetric analysis (TGA): The thermal stability of synthesized polymer can be evaluated by thermo-gravimetric analysis. The TG curves of the samples were analyzed as a function of soft segment and relationships between the degrees of the physical cross-linking [20]. Fig. 5 showed the decomposition temperature of prepared SMPUs for different percentage by weight loss. It is clear from the available data that prepared samples have a regular trend of thermal stability with significant difference of onset temperature, while, a little difference of T_{max} has also been observed. The temperature for different percentage of weight loss (on set, 5, 10, 20, 50 % and max.) is presented in Table-2. It can be observed from shifting of onset temperature from 231 to 277 °C that the thermal stability of SMPUs increases with the increasing PCL molecular weight and the sample prepared with 4000 g/mol PCL has the maximum thermal stability. It means the length of soft segments has considerable effect on the thermal stability of the prepared samples.

It is well known that usually the hard segments undergo early stage degradation while urethane depolymerized to monomers and carbon dioxide [21]. The TGA studies showed that the degradation start at about 231 °C and ended at 593 °C with formation of char. This phenomenon also suggested that more the soft segments length, the more the intermolecular polar interaction, increasing urethane groups and showed high stability.

Differential scanning calorimetric (DSC) analysis: The shape fixity and recoverability can be controlled by glass transition (T_g) of the amorphous phase [22]. It was investigated that both the degree of crystallinity and transition temperature would be altered in the presence of different molecular weight of the PCL. The thermal behaviour of each sample of shape memory polyurethane was studied by DSC. The cooling and heating traces of DSC thermograms are shown in Figs. 6 and 7, respectively. The results for all SMPUs as glass transition temperature (T_g) and crystallization temperature (T_c) for both cooling and heating scans, with their respective enthalpies (ΔH), are summarized in Table-3. The peaks of SMPU1-SMPU6 had T_g ranging from -55.69 to 70.29 °C with corresponding enthalpies (0.13 to 0.35 J/g). The curve belonging to SMPU7 & SMPU8 showed T_g and T_c both in cooling and heating scans (Figs. 6 and 7). In heating curve, SMPU7 showed transition peaks at -55.69 °C (T_g), -9.66 °C (T_c) and 42.72 °C (T_m), with corresponding enthalpies 0.315 J/g, 22.89 J/g and -42.43 J/g, respectively. While SMPU8 had 0.35 J/g, -42.43 J/g (ΔHm) heat release for -53.74 °C (T_g) and 45.38 °C (T_m).

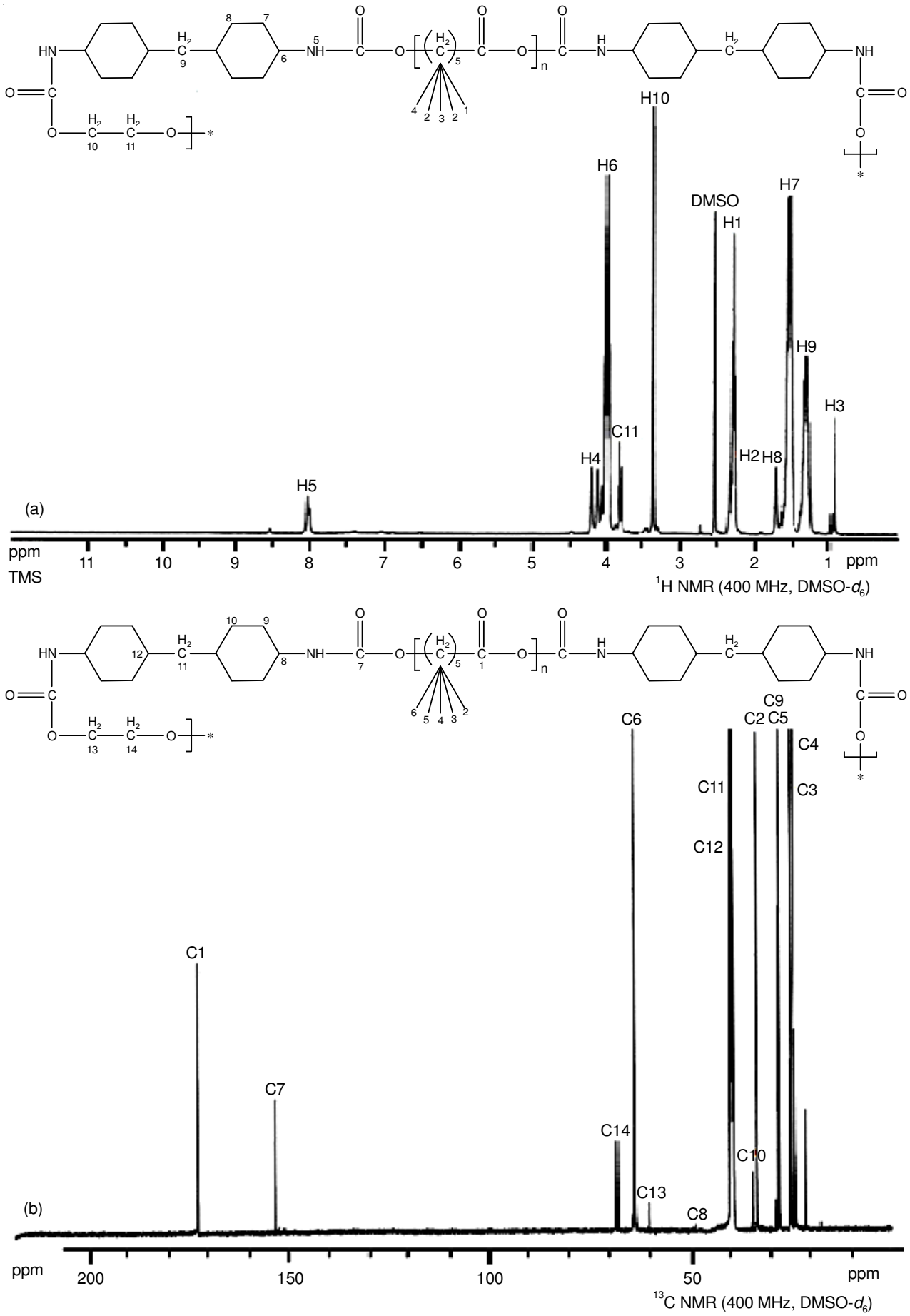

Fig. 4. (a) ^{1}H NMR (b) ^{13}C NMR spectra of polyurethane extended with 1,2-ethanediol (SMPU6)

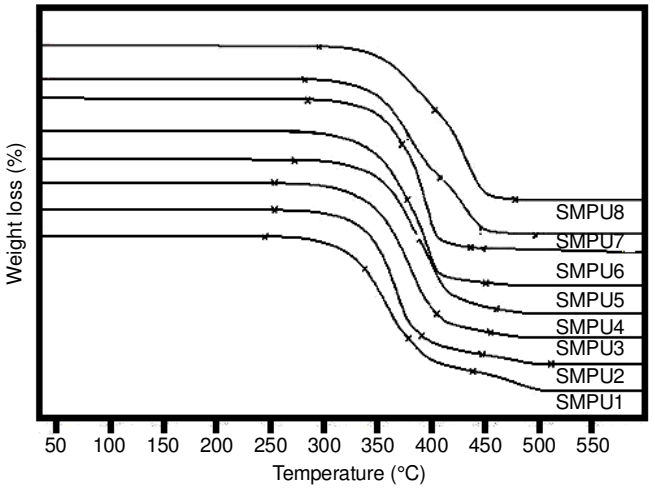

Fig. 5. Comparative presentation of percentage weight loss of different SMPU samples

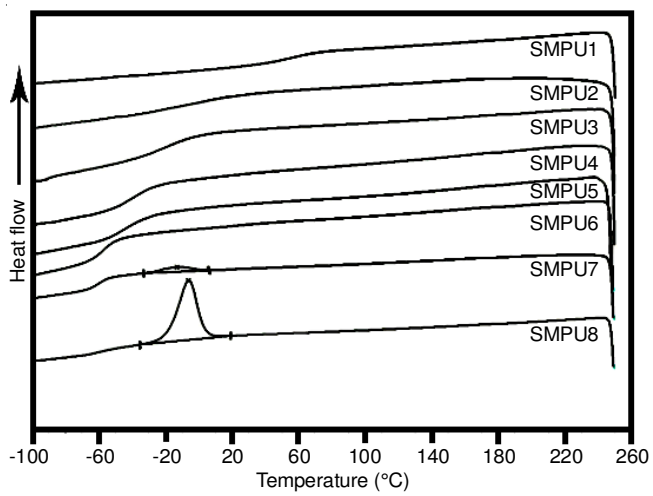

Fig. 6. Cooling DSC thermogram (10 °C/min) of SMPU samples

It was found that all SMPUs showed only one glass transition temperature (T_g) at same position in both 2nd heating and cooling scan. The fact that only one T_g detected indicates apparent compatibility segments in the amorphous state [23]. The absence of any secondary transition in cooling scan indicates an amorphous region as well [24]. It was revealed that SMPUs with high molecular weight of PCL also showed the crystallization transition (T_c) and melting transitions (T_m). It was noticed that enthalpy change of soft segments (ΔHm.s) was also increased with increasing PCL chain length, due to higher degree of crystallinity of soft segments.

Moreover, the glass transition temperature (T_g) presented in Table-3 showed the decreasing trend of the glass transition temperature with increasing molecular weight of polycaprolactone diol. For example, the T_g values obtained for increasing molecular weight of PCL blocked H_{12}MDI were 70, 7.92, -11.46, -36.16, -38.41, -53.73, -55.69 and -53.74 °C. The decreasing trend may be explained due to the increase in chain lengthening and flexibility behaviour of –NHCOO– linkage formed during the reaction, which in turn decreased the physical crosslinking [25]. The reduction of T_g was associated with presence of excess free volume in the matrix system.

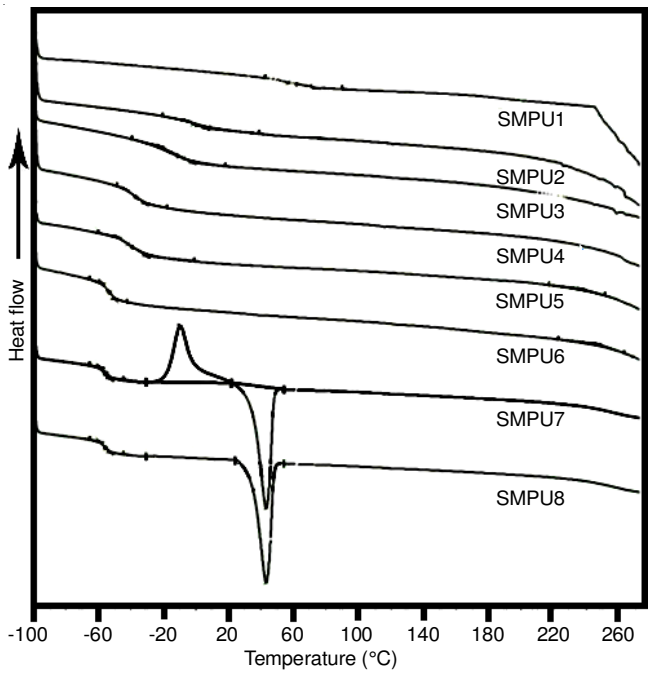

Fig. 7. 2nd heating DSC thermogram (10 °C/min) of SMPU samples

Dynamic mechanical thermal analysis (DMTA): The viscoelastic properties are the most important parameter for understanding the molecular behaviour of polymers, so DMTA is helpful in detecting various types of transitions related to morphology of the samples. The storage modulus and tan δ values as functions of temperature are shown in Figs. 8 and 9. The stiffness and elasticity of the final samples can be determined by storage modulus. Moreover, it is helpful to find out service temperature range also.

It is obvious from the Fig. 8 that increase in soft segments length resulted a change in the thermal transition of final SMPU. The polymer with lowest molecular weight of PCL (SMPU1) had low temperature range and low plateau modulus as compared to other samples. This showed the high molecular rigidity of SMPU1 ($\bar{M}_n$ 400 g mol^{-1}) among other samples, which might useful to determine the physical properties of synthesized sample. The plateau modulus continuously increased with increasing PCL molecular weight in soft segment.

On the other hand, the higher value of plateau modulus along with wider temperature range (SMPU8) suggested the increasing strength of polymer with increasing molecular weight of polyol. While no significant change was observed below glass transition temperature (T_g). The decrease of modulus was associated with T_g. The SMPU8 modulus decrease rapidly as compared to SMPU1 having low crystallinity [26]. It is well known that the glass transition temperature of soft segments is attributed to α transition in tan δ curves in DMTA and can be used as sign of the degree of phase separation.

It is considered that the heat treatment and polymer stress have great influence on both degree of crystallinity and molecular orientation. The structural difference *i.e.*, lengths of soft segments have deep effects on the dynamic mechanical properties. It was observed from tan δ curves (Fig. 9), the glass transition temperature appeared at wide temperature range for all peaks; which might be affected by molecular and

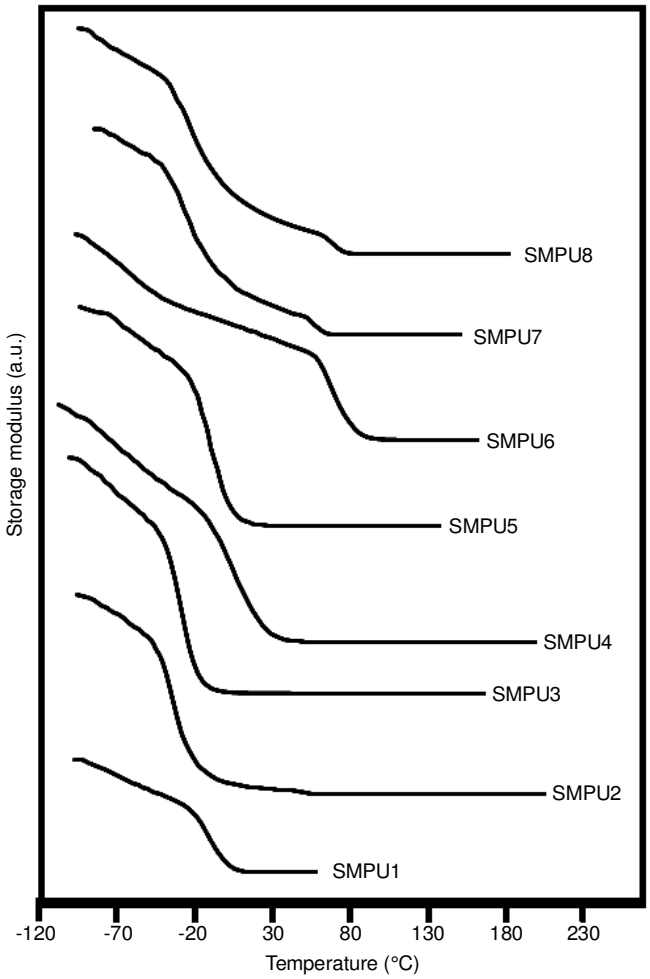

Fig. 8. Storage modulus/temperature curves of SMPU samples

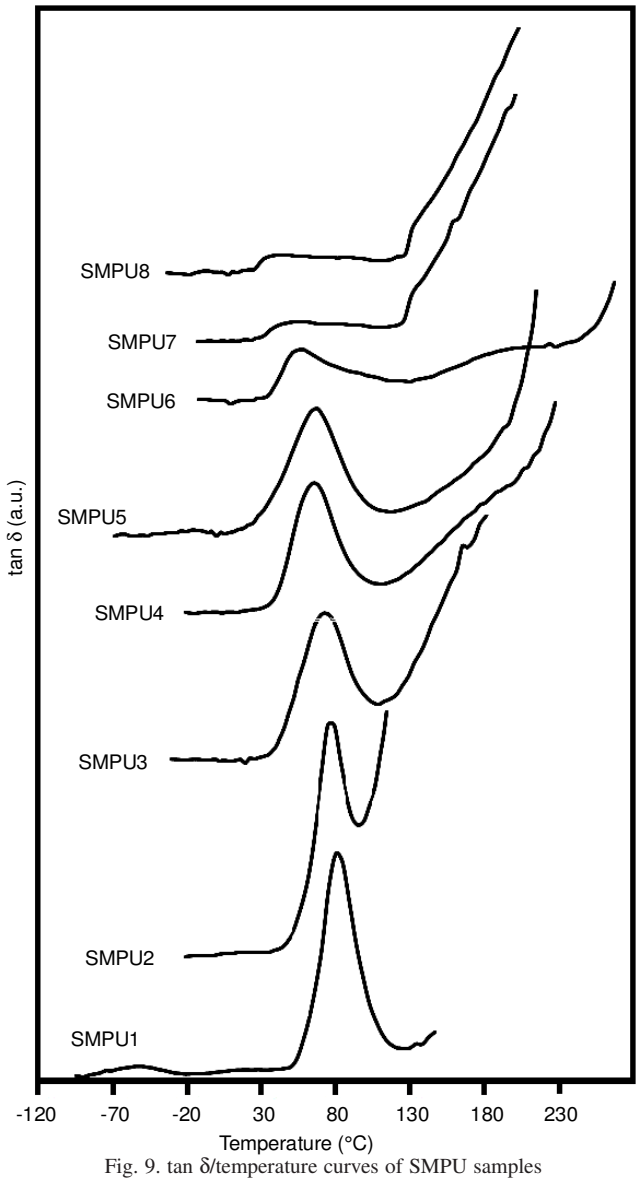

Fig. 9. tan δ/temperature curves of SMPU samples

chemical structure like flexibility and polarity of attached groups. The intensity and peaks broadness was also found to be decreased with increasing PCL molecular weight. The T_g can also be interpreted by studying damping peaks height and increasing length of soft segments.

The increasing molecular weight of PCL resulted, decreasing damping peaks height and energy dissipation of polymers [27]. The T_gs of the prepared polymer move toward lower temperature as the molecular weight increases. The tan δ peak located at about +70 °C (SMPU1) shifted to about -55 °C (SMPU8) as the molecular weight of polyol increased. The decrease in T_gs, smaller tan δ peaks with increasing PCL molecular weight was attributed to increasing crystallinity of synthesized polymers. The dereasing intensity of damping peaks with increasing degree of crystallinity can be explained by following equation [28]:

$$\tan \delta = W_c (\tan \delta)_c + (1\text{-}W_c)(\tan \delta)_a$$

where 'a' and 'c' refer to the contributions of amorphous and pure crystalline phases, respectively. The tan δ equation for the maximum peak can be simplified as

$$\tan \delta \cong W_c (1\text{–}W_c)(\tan \delta)_a$$

The present study showed the decreasing tan δ trend.

Shape memory effect: The vital parameter such as shape recovery and fixity was evaluated to determine shape memory performance of the polymers. In this study, these parameters were investigated as function of deformation conditions. Shape recovery and retention of polymers were carried out around T_m of soft segment. Shape recovery was increased from 79 % of SMPU1 to 91 % of SMPU8 (Table-4). The shape recovery of SMPU1 was found smallest and slightly increased as molecular weight of PCL increased. The samples with low molecular weight of PCL showed same recovery percentage after that with the increasing length of soft segment, the recovery rate increased. This improvement is due to increase in crystallinity of polymer. This high value of shape recovery is competitive to previous studies [29,30].

The SMPU8 can be classified as the best, as judge from the point that shape recovery above 90 % is very hard to reach as compared to the previous excellent SMPUs [29]. The reason for the amazingly high shape recovery could be employment of longer PCL and its increasing flexible linking. Shape retention of prepared samples varied from 59 to 79 %. As it can be observed that the shape fixity increased with correspondingly increasing strain amplitude, which may be due to the orientation of soft segments in higher molecular weight PCL. It can be observed that the strain amplitude is correlated to soft segment mobility.

TABLE-4
CYCLIC TENSILE BEHAVIOUR OF SMPU SAMPLES

Sample code	Shape recovery (%)	Shape retention (%)
SMPU1	70	59
SMPU2	75	62
SMPU3	75	65
SMPU4	78	69
SMPU5	80	72
SMPU6	86	75
SMPU7	87	76
SMPU8	91	79

Shape retention values were found to be decreased if the shape recovery force was strong even at -50 °C. The shape retention of SMPU8 was less (79 %) as compared to shape recovery (91 %). This decreased shape retention did not discourage the investigation of long chain soft segments SMPUs, because a recovery above room temperature could be attained by high molecular weight PCL.

Conclusion

In present study the SMPUs series has been synthesized by varying molecular weight of polycaprolactone diol and their thermal, mechanical and thermo-mechanical properties were characterized. The FT-IR spectroscopy showed that the increase of molecular weight of polyol, can effect on both physical crosslinking and intermolecular interaction forces. It also confirm the completion of the reaction of –NCO and –OH groups. The thermal analysis has showed that the length of soft segments effect the melting temperature along with respective enthalpy of soft segments. In addition, it showed that with the increase in length of soft segment not only the thermal stability but also the crystallinity of prepared samples increased. The appearance of signal thermal transition revealed the amorphous region but also showed significant effect of phase separation and crystallinity with increasing length of soft segments. Moreover, the decrease in T_g interpreted in term of increasing phase separation and chain flexibility with increasing PCL length, which has been confirmed by DMTA, where damping peaks were affected by the increasing length of soft segments. Finally the shape memory test concluded that the increase in molecular weight of PCL also showed increasing trend in shape recovery and good retention values as well. On the basis of these results, it can be said that, the sample SMPU8 having PCL ($\overline{M}_n$ 4000 g mol^{-1}) showed 91 % shape recovery with 79 % shape retention.

ACKNOWLEDGEMENTS

The present data is the part of Ph.D. thesis of Ms. Shazia Naheed. It is highly acknowledged and appreciated the support of Higher Education Commission (HEC), Pakistan, Iran Polymer and Petrochemical Institute (IPPI), Tehran, Iran and Perstorp Polyols (Solvay Chemicals, Inc. Toledo, Ohio) to accomplish this research.

REFERENCES

1. K.M. Zia, H.N. Bhatti and I. Ahmad Bhatti, *React. Funct. Polym.*, **67**, 675 (2007); https://doi.org/10.1016/j.reactfunctpolym.2007.05.004.
2. M. Alexandru, M. Cazacu, M. Cristea, A. Nistor, C. Grigoras and B.C. Simionescu, *J. Polym. Sci.*, **49**, 1708 (2011); https://doi.org/10.1002/pola.24602.
3. T.H. Kang, J.M. Lee, W.R. Yu, J.H. Youk and H.W. Ryu, *Smart Mater. Struct.*, **21**, 035028 (2012); https://doi.org/10.1088/0964-1726/21/3/035028.
4. H. Meng and Jinlian Hu, *J. Intell. Mater. Syst. Struct.*, **21**, 859 (2010); https://doi.org/10.1177/1045389X10369718.
5. J.T. Kim, B.K. Kim, E.Y. Kim, H.C. Park and H.M. Jeong, *React. Funct. Polym.*, **74**, 16 (2014); https://doi.org/10.1016/j.reactfunctpolym.2013.10.004.
6. G. Chen, Y. Ma, X. Zheng, G.A. Xu, J. Liu, J. Fan, D. Shen and Z. Qi, *J. Polym. Sci. B*, **45**, 654 (2007); https://doi.org/10.1002/polb.21075.
7. B.S. Lee, B.C. Chun, Y.C. Chung, K.I. Sul and J.W. Cho, *Macromol.*, **34**, 6431 (2001); https://doi.org/10.1021/ma001842l.
8. J.T. Kim, B.K. Kim, E.Y. Kim, H.C. Park and H.M. Jeong, *React. Funct. Polym.*, **74**, 16 (2014); https://doi.org/10.1016/j.reactfunctpolym.2013.10.004.
9. J. Hu, Z. Yang, L. Yeung, F. Ji and Y. Liu, *Polym. Int.*, **54**, 854 (2005); https://doi.org/10.1002/pi.1785.
10. B. Yang, W.M. Huang, C. Li, C.M. Lee and L. Li, *Smart Mater. Struct.*, **13**, 191 (2004); https://doi.org/10.1088/0964-1726/13/1/022.
11. M. Behl, M.Y. Razzaq and A. Lendlein, *Adv. Mater.*, **22**, 3388 (2010); https://doi.org/10.1002/adma.200904447.
12. H. Lu, Y. Liu, J. Leng and S. Du, *Eur. Polym. J.*, **46**, 1908 (2010); https://doi.org/10.1016/j.eurpolymj.2010.06.013.
13. M. Szycher, Handbook of Polyurethanes, CRC Press, New York, edn 2 (2013).
14. T. Xie, *Polymer*, **52**, 4985 (2011); https://doi.org/10.1016/j.polymer.2011.08.003.
15. I.M. Pereira and R.L. Orefice, *Polymer*, **51**, 1744 (2010); https://doi.org/10.1016/j.polymer.2010.02.037.
16. L.H. Chan-Chan, R. Solis-Correa, R.F. Vargas-Coronado, J.M. Cervantes-Uc, J.V. Cauich-Rodríguez, P. Quintana and P. Bartolo-Pérez, *Acta Biomater.*, **6**, 2035 (2010); https://doi.org/10.1016/j.actbio.2009.12.010.
17. ASTM, Standard American Society of Testing Material, ASTM International, USA (2004).
18. M. Barikani, K.M. Zia, I.A. Bhatti, M. Zuber and H.N. Bhatti, *Carbohydr. Polym.*, **74**, 621 (2008); https://doi.org/10.1016/j.carbpol.2008.04.023.
19. M.K. Hur, J.M. Kwak and T. Hur, *Polymer (Korea)*, **20**, 392 (1996).
20. P.S. Thomas, J.P. Guerbois, G.F. Russell and B.J. Briscoe, *J. Therm. Anal. Calorim.*, **64**, 501 (2001); https://doi.org/10.1023/A:1011578514047.
21. U. Sebenik and M. Krajnc, *Colloids Surf. A Physicochem. Eng. Asp.*, **233**, 51 (2004); https://doi.org/10.1016/j.colsurfa.2003.11.021.
22. E.-S.M. Negim, L. Bekbayeva, G.A. Mun, Z.A. Abilov and M.I. Saleh, *World Appl. Sci. J.*, **14**, 402 (2011).
23. X. Gu and P.T. Mather, *Polymer*, **53**, 5924 (2012); https://doi.org/10.1016/j.polymer.2012.09.056.
24. P. Singhal, W. Small, E. Cosgriff-Hernandez, D.J. Maitland and T.S. Wilson, *Acta Biomater.*, **10**, 67 (2014); https://doi.org/10.1016/j.actbio.2013.09.027.
25. D. Shi, M. An and G. Wang, *Int. J. Chem.*, **1**, 48 (2009); https://doi.org/10.5539/ijc.v1n2p48.
26. K.M. Zia, M. Barikani, M. Zuber, I.A. Bhatti and H.N. Bhatti, *Iran. Polym. J.*, **17**, 61 (2008).
27. K.M. Zia, M. Barikani, I.A. Bhatti, M. Zuber and H.N. Bhatti, *J. Appl. Polym. Sci.*, **109**, 1840 (2008b); https://doi.org/10.1002/app.28242.
28. T. Myrayama, Dynamic Mechanical Analysis of Polymeric Material, Elsevier, Amsterdam (1978).
29. B. Yan, S. Gu and Y. Zhang, *Eur. Polym. J.*, **49**, 366 (2013); https://doi.org/10.1016/j.eurpolymj.2012.09.026.
30. Y.C. Chung, J.W. Choi, J.M. Jung and B.C. Chun, *Fibers Polym.*, **10**, 743 (2009); https://doi.org/10.1007/s12221-009-0743-z.