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Synthesis and characterisation of soluble block copolymers from NR and TDI based polyurethanes

M. N. Radhakrishnan Nair · M. R. Gopinathan Nair

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Abstract Soluble block copolymers from toluene diisocyanate (TDI), with chain extender diols, viz., propylene glycol (PG), 1,4-butane diol (1,4-BDO) and 1,3-butane diol (1,3-BDO), were synthesised for the first time by solution polymerisation. Maintaining low hard segment content and keeping optimum NCO/OH ratio, formation of linear, flexible elastomers is achieved. They were characterised by spectral, thermal, microscopic and stress–strain analysis. The dilute solution properties of these block copolymers dissolved in tetrahydrofuran (THF) are studied by viscometry and gel permeation chromatography (GPC). IR and NMR spectral data support the notion that a chemical reaction leads to block copolymerisation. Differential scanning calorimetric (DSC) analysis showed a soft segment glass transition temperature around –58°C and a hard segment glass transition temperature between 75 and 70°C for these samples. This observation and two-stage thermal decomposition of the samples in thermogravimetric analysis (TGA) clearly indicate that the block copolymers are completely phase-segregated systems. SEM indicates the amorphous heterophase morphology of the samples.

Introduction

In the past couple of decades, scientific and technological developments have evolved with particular emphasis on production of ecofriendly materials from renewable resources. Modifying natural rubber is an interesting proposal, due to its ecofriendly characteristics. Out of the several ways of modification of NR, block copolymerisation offers a method of modifying the rubber chemically. Our laboratory has been investigating the possibility of developing new polymeric materials from natural rubber. This has led to the synthesis of natural rubber based block polymers [1–5]. Among them, the copolymers based on NR and polyurethanes are known to exhibit elastomeric properties. This property of segmented polyurethane block copolymers arises from the microphase segregation between incompatible rubbery soft segment and glassy hard segment sequences. The glassy hard polyurethane segments constitute the hard domain, which functions as thermally labile cross-link sites and filler for the rubbery soft segment matrix. As an entity, block copolymers retain the major advantages of both the constituent blocks. A wide range of physical and morphological properties can be obtained, depending upon the composition and chemical structure of the hard segments in the block copolymer structure [6–15]. The hard and soft segments in block copolymers are thermodynamically incompatible, and the polymer undergoes microphase segregation, which has a great influence on the polymer properties [16–17]. The soft segment provides elastomeric character for the polymer, while hard the segment provides dimensional stability. Number of attempts have been made to establish relation between morphology, hard segment content, synthesis conditions, thermal treatment and physical properties [18, 19] of PUs. Many authors observed [20, 21] that better properties could be achieved when the microphase segregation between soft and hard segment increases.

Block copolymers of conjugated polydienes have been the subject of active research during the past couple of decades. Among the polydienes, polybutadiene (PB) is the

M. N. Radhakrishnan Nair
Department of Chemistry, D.B. College Thalayolaparambu,
Kottayam 686605, Kerala, India

M. R. Gopinathan Nair (✉)
School of Chemical Sciences, Mahatma Gandhi University,
Priyadarshini Hills, Kottayam 686560, Kerala, India
e-mail: mrg.nair@rediffmail.com

one used for most of these studies [22, 23]. The complete hydrocarbon nature of PB prevents formation of intersegment hydrogen bonds, [24] which are usually present in polyester, or polyether based PUs favouring phase segregation. Polyether–PU copolymers of the 4,4′-diphenylmethane/1,4-butane diol system and their properties in relation to hard segment content, length and distribution have been studied extensively [25]. Various segmented PU material with PU hard segment content of 40% were prepared from a poly(tetramethylene ether) glycol with 1,2-butane diol of $\overline{M}_n$ = 2,000 and various diisocyanates, including, 2,4-toluene diisocyanate, isophorone diisocyanate, hydrogenated 4,4′-diphenylmethane diisocyanate (MDI), pure MDI and 1,6-hexane diisocyanate. The degree of inter-urethane hydrogen bonding and the enthalpy of hydrogen bond dissociation have been used as indicators of phase separation in MDI PU segmented elastomers. The strength and elasticity of PUs are due to the hard domains stabilised by the hydrogen bonding between hard segments. Studies [26] have been conducted on MDI-butane diol (BDO) systems. Synthesis and characterisation of the block copolymers based on PB have been reported during this period. All the samples of this block copolymer synthesised so far lack solubility, but swell in suitable solvents. The main purpose of synthesising block copolymers from these components was to use them as thermoplastic elastomers (TPEs). However, the lack of solubility and also fusibility caused limitation to their use as a thermoplastic material.

Generally, segmented block copolymers based on polyurethanes are found to lack solubility irrespective of the nature of soft segments involved. Hence, the insolubility is presumed to be due to the cross linking in the polyurethane segments. Studies in our lab showed that it is possible to synthesise polyurethane segments devoid of crosslinks. In this context, the present work was undertaken with a view to synthesise soluble block copolymers from NR and PU. The present work is an attempt to synthesise and characterise a series of soluble block copolymers of NR and polyurethane using different short chain aliphatic diols as chain extenders. Solution properties of block copolymers derived from 1,3-butane diol with a view to study the chain conformation of the block copolymers with three different NCO/OH ratios has been reported [27]. This contribution is an attempt to report findings after carrying out more work on the subject involving different routs of synthesis with different chain extender diols, and elaborate studies on product characterisation.

Experimental

Materials

Natural rubber (ISNR-5): viscosity average molecular weight (M_v) = 8.2×10^5, intrinsic viscosity [η] in benzene at 30°C = 4.45 dl/g, Wallace plasticity, P_0 = 39.0. It was obtained from Rubber Research Institute of India (RRII), Kottayam, Kerala. Toluene diisocyanate (TDI) was an 80/20 mixture of 2,4- and 2,6-isomers. This was supplied by Merck (Germany) and used as received. Propylene glycol (PG) obtained from E.Merck, India and 1,4-butane diol (1,4-BDO) supplied by Fluka (Switzerland). 1,3-Butane diol (1,3-BDO) was supplied by Riedel-dettaën (Germany). These diols dried with anhydrous CaO, and then distilled under reduced pressure before use. Dibutyl tin dilaurate (DBTDL) was supplied by Fluka (Switzerland), and used as catalyst without further purification. Chloroform was laboratory grade, which was supplied by Merck India Ltd., Bombay (India). It was dried with anhydrous calcium oxide, and then distilled before use. Methanol (reagent grade) was obtained from Merck India Ltd. It was used without further purification. Hydrogen peroxide (30%) was obtained from Merck India Ltd. Toluene and tetrahydrofuran (THF) (reagent grade) supplied by Merck India Ltd. was distilled before use.

Hydroxyl terminated liquid natural rubber (HTNR) of number average molecular weight 4,600 was prepared in the laboratory by the photochemical degradation of natural rubber as per reported procedure [28]. It was reprecipitated thrice from toluene using methanol and dried at 70–80°C in vacuum.

Synthesis of block copolymers

The composition of the block copolymer samples prepared in this study is presented in Table 1. The overall composition for the synthesis of various block copolymers was calculated in molar ratios of the respective reactants. For all the samples, the PU hard segment content is kept around 30%. For example, the overall composition for the synthesis of [NR/PU]-1 is 1.00/8.51/7.88, which is the ratio of the number of moles of HTNR, TDI and PG. The above ratio was calculated as follows on the assumption that the reaction between PG and TDI is fast and instantaneous under the given reaction conditions. The number average molecular weight of HTNR was determined by gel permeation chromatography to be 4,600. Molecular mass of polyurethane required for NR/PG (70/30) is (30/70) × 4,600 = 1,971.42. This mass of PU is constituted by 1,971.42 × 76/(76 + 174.16) = 598.93 g or 7.88 mol of PG, and 1,971.42 × 174.16/(76 + 174.16) = 1,372.49 g or 7.88 mol of TDI, where 76 and 174.16 are the molecular weights of PG and TDI, respectively. This would yield hydroxyl terminated PU chains of the required molecular weight. Additional 2 mol of TDI were required to end cap HTNR with isocyanate groups. Thus the total number of moles of TDI required = 7.8806 + 2 = 9.88 mol = 1,720.6 g. It is expected that at this higher molar

Table 1 Composition of NR/PU block copolymers

Sample	NCO/OH ratio	Molar proportion of reactants	wt% hard segment	wt% soft segment
(NR/PU)-1	1.08	HTNR/TDI/PG 1/8.51/7.88	31.14	68.86
(NR/PU)-2	1.08	HTNR/TDI/1,4-BDO 1/8.51/7.88	31.88	68.12
(NR/PU)-3	1.08	HTNR/TDI/1,3-BDO 1/8.51/7.88	31.88	68.12

concentration of isocyanate reaction could yield PU chains of unspecified higher molecular weight. Hence, the growth of the chain is to be restricted to the required range by using a lower NCO/OH ratio (in this study, it is chosen as 1.08 based on a large number of trials), i.e. $7.88 \times 1.08 = 8.51$. Now the weight percentage of hard segment (PU) = $[(1{,}482.10 + 598.93)/(1{,}482.10 + 598.93 + 4{,}600)] \times 100 = 31.14\%$. An excess of 2% of TDI (equal to 0.17 mol) was added to compensate any loss during transfer and side reactions. Similar calculation was adopted for other compositions as well. Thus, the calculated values % of the polyurethane content of different samples of the block copolymers work out to be 31.14, 31.88 and 31.88, respectively for the [NR/PU]-1, [NR/PU]-2 and [NR/PU]-3.

The apparatus consisted of a 250-ml conical flask, stirring paddle and reflux condenser. Polyurethane oligomers were prepared by dissolving stochiometric amount of the respective diol in chloroform to get a 10% solution. The catalyst, viz., DBTDL (0.5% by weight of the TDI) was added to the diol solution. After maintaining the temperature of the system at 65°C, a 10% solution of TDI in chloroform was added within 5 min to the reaction mixture. Heating was continued for 60 min. After that, a fixed quantity of HTNR (8 g) as a 20%, w/v solution in chloroform was added to the reaction mixture with stirring at a temperature of 65°C. The reaction was carried out for 5 h. Then excess of solvent was distilled off, and the viscous polymer solution was cast in trays treated with silicon release agent. The solid polymer was removed from the tray and kept at 60°C in a vacuum oven for 12 h for removing any residual solvent followed by 2 weeks ageing at room temperature in a dry atmosphere. In all the cases, the NCO/OH ratio is maintained at 1.08.

Polymer designation

Samples of block copolymers are designated as [NR/PU]-1, [NR/PU]-2 and [NR/PU]-3, representing NR-b-PU (PG), NR-b-PU (1,4-BDO) and NR-b-PU (1,3-BDO), respectively.

Measurements

Gel permeation chromatography (GPC)

Molecular weight was determined by GPC using a simple calibration based on polystyrene standard on a Shimadzu LC4A (Japan). GPC system was equipped with a refractive index detector. THF was used as the eluent at a flow rate of 1 ml min^{-1} at 27°C.

IR spectra were recorded at room temperature on a Shimadzu FTIR-8400S, spectrometer (Japan) by averaging 50 scans at a resolution of 2 cm^{-1}.

^{1}H-NMR spectra were recorded at room temperature using AMX-400 NMR spectrometer (Japan) at operating frequency 400 MHz using DMSO as solvent. ^{13}C-NMR spectra were recorded at room temperature using AMX-400 spectrophotometer at operating frequency 100 MHz using DMSO as solvent.

Differential scanning calorimetry (DSC)

The DSC measurements were done using a Shimadzu DSC60 thermal analyser (Japan) at a programmed heating rate of 10°C/min. The experiments were carried out in the temperature range, 30–300°C under dry nitrogen atmosphere (25 ml/min) using alumina crucibles. The sample weight was 4–5 mg. For measuring sub ambient transition, the DSC was performed with a Mettler Inc. (TA 300) micro calorimeter (Germany).

Dilute solution viscosity measurement

Stock solutions of the polymers were prepared using pure and filtered THF solvent at least 1 day before measurement. These solutions were filtered before use. The amount of polymer lost was assumed to be negligible. Standard solutions of each sample were prepared from the stock solutions whose concentration was about 2%, by serial dilution to get 0.25 wt% solutions. Viscosity measurements were carried out using an Ubbelohde viscometer at room temperature in a thermostat condition. The flow time was measured in triplicate for each concentration (measured to 1% accuracy depending on flow time) to determine the intrinsic viscosity.

Stress–strain behaviour

Stress–strain behaviour was studied on a Zwick 1474 Universal Testing Machine (Germany) as per ASTM D

412-80 test method at a constant cross head speed of 500 mm/min. Five dumb-bell shaped specimens of every sample were used to determine the Young's modulus, tensile strength and elongation at break and the average value was taken as the result.

Scanning electron microscopy (SEM)

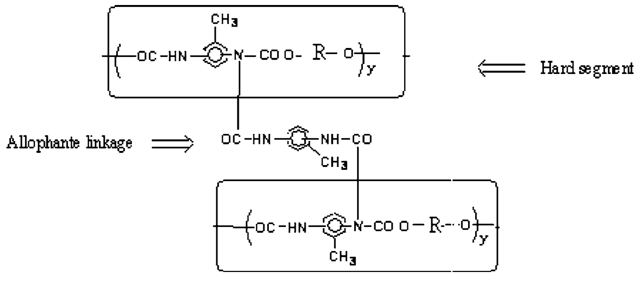
The cryogenically fractured surfaces of thin films were examined using a JEOL 5400, SEM (Tokyo, Japan) at 20 kV using magnifications 500–3,000 to study the morphology of the samples. The surface was sputter coated with Au/Pd alloy in a sputter coating machine (Balzers SCD 050, Germany). A minimum of five photographs were taken for each sample for analysis.

Results and discussion

Earlier works in our laboratory showed that the NR/PU block copolymer properties strongly depended on the NCO/OH ratio used in the synthesis. Usually, polyurethane becomes cross-linked because of allophanate linkage that occurs in the presence of excess diisocyanate (Scheme 1). At an optimum NCO/OH ratio, the NCO concentration reduces to such a level that uncross-linked polyurethane chains are formed which undergo chain extension with the HTNR to give the soluble block copolymer. Soluble products with NCO/OH ratio of 1.08 are synthesised and their characterisation is discussed in this section. The compositions of the samples studied is summarised in Table 1.

IR spectra

The IR spectra of HTNR, NCO end capped HTNR, polyurethane oligomer prepared from TDI and PG and the block copolymers (NR/PU)-1 to (NR/PU)-3 are given in Fig. 1a–e. Peak assignments have been done and the data are tabulated in Table 2. The band at 3,400–3,600 cm^{-1} in Fig. 1a represents the hydroxyl group in HTNR. This band disappears in Fig. 1b and new band at 3,200 and 2,260 generate. This represents the >N-Hand –NCO groups, respectively and indicate complete endcapping of HTNR with TDI. The IR spectra of the (NR/PU)-1 (Fig. 1d) has got all the features of the HTNR spectrum in Fig. 1a and the polyurethane spectrum in Fig. 1c. PU contains proton donor group (NH) and proton accepter group (C=O). Therefore, hydrogen bonding between hard segments can exist [6, 7]. Hydrogen bonding has significant effect on the physical properties of PU. Hydrogen bonded NH peak in infrared spectra displays frequency shift, changes in intensity and bandwidth. The band between 3,400 and 3,300 cm^{-1} is due to the NH bond in the PU. A very weak shoulder occurs around 3,360 cm^{-1} indicating the presence of a few number of free NH groups. In the carbonyl region, the band around 1,700 cm^{-1} is found to be very strong. Additional peaks at 1,600 and 1,534 cm^{-1} are attributed to stretching vibrations of C=C bond in aromatic ring and bending mode of NH bond, respectively. NH absorption bands for all the synthesised block copolymers are found at 3,378–3,354 cm^{-1}. The IR spectra show typical bands in the carbonyl (C=O) vibration region (1,707–1,704 cm^{-1}), which are attributed to the urethane group, and a band around 1,600 cm^{-1}, which is assigned to the C–C double bond. Thus, all the characteristic absorption bands of NR and PU are presented in the spectra of block copolymers indicating the block copolymer structure. It is found that all the block copolymers based on the various diols exhibit all the characteristic features of the NR soft segments and the polyurethane hard segments, which are summarised in Table 2.



Scheme 1 Allophanate linkage in cross-linked block copolymers

NMR spectra

^{1}H-NMR and ^{13}C spectra of HTNR, PU oligomer of the block copolymer [NR/PU]-3 and the block copolymers are given in Figs. 2a–e and 3a–c, respectively. The ^{1}H-NMR and ^{13}C spectra of the block copolymers support the IR spectra in the characterisation of the soft and hard segments. Both the spectra give all peaks characteristic of the NR soft segments and the respective hard segments. NMR spectrum of HTNR is shown in Fig. 1a. The resonances at 2.03 ppm (H_1), 1.67 ppm (H_3) and 5.12 ppm (H_2) are characteristic of isoprene unit. In the ^{1}H-NMR spectrum of a representative PU oligomer, viz., of NR/PU-3 (Fig. 1b), the aromatic protons give a multiplet around 7.26 ppm (H_5, H_6 and H_7). The amino protons resonate at 4.42 ppm (H_4). The benzylic protons (H_8) resonate at 2.18 ppm. The methyl protons (H_{12}) resonate at 1.87 ppm. The methylene protons (H_{10}) and (H_{11}), resonate at 1.81 and 3.7 ppm, respectively. The tertiary proton (H_9), resonate at 4.21 ppm. ^{1}H-NMR spectrum of the reactants HTNR and PU is contained in the

Fig. 1 IR spectrum of (**a**) HTNR, (**b**)-NCO endcapped NR, (**c**) PU hard segment of [NR/PU]-1, (**d**) [NR/PU]-1, (**e**) [NR/PU]-2 and (**f**)[NR/PU]-3 block copolymers

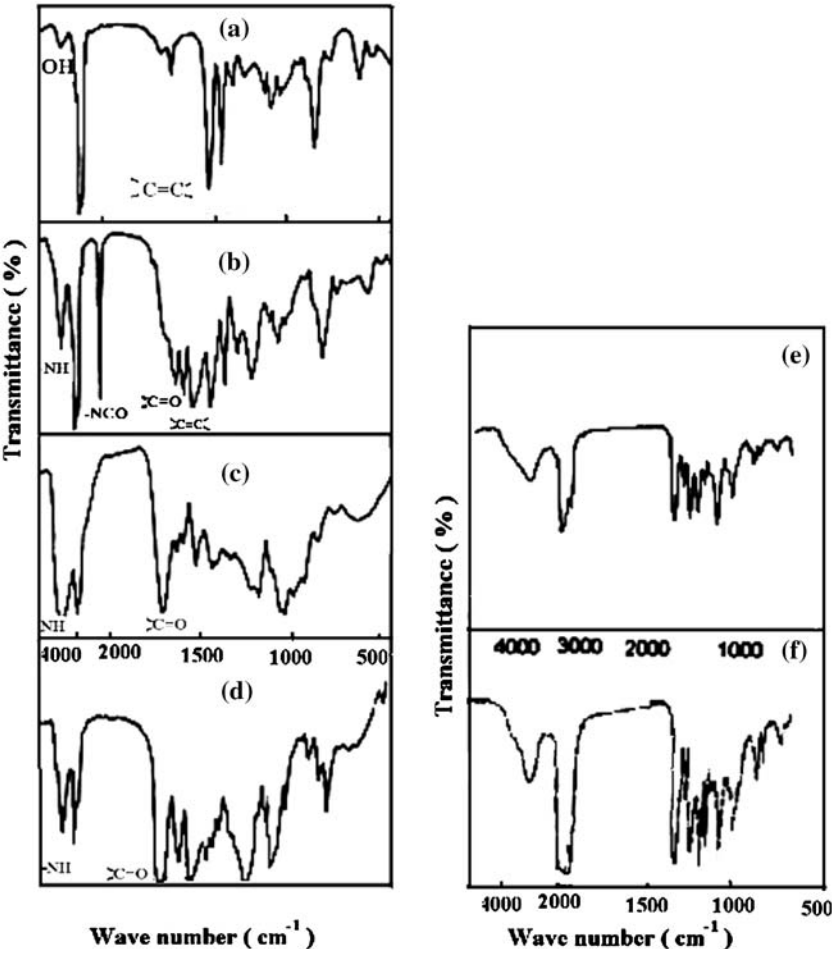


Table 2 Peak assignment in the IR spectra of block copolymers

(NR/PU)-1	(NR/PU)-2	(NR/PU)-3	HTNR	PU	Main peak assignments
			3,600–3,400		v (OH)
3,360	3,378	3,354		3,364	v (N–H), free N–H
3,310	3,312	3,303		3,304	v (N–H), bonded N–H
2,965	2,965	2,959	2,959	2,970	v s (CH_2)
2,928	2,929	2,919	2,919		v s (CH_2)
2,853	2,856	2,853	2,853		v s (CH_2)
1,707	1,714	1,713		2,248	v (C=O), bonded C=O
1,631	1,634	1,624	1,664	1,708	v (C=C), alkene
1,601	1,610	1,600			v (C=C), aromatic ring
1,532	1,548	1,527		1,603	v (N–H) + v (C–N)
1,444	1,460	1,447	1,454	1,537	v (CH_2)
1,375	1,377	1,374	1,375	1,452	v (CH_2)
1,329	1,312	1,321			v (N–H) + v (C–N)
1,231	1,233	1,229	1,242	1,234	v (CH_2)
1,138	1,144	1,123		1,134	v (N–H) and v (C–N)
1,069	1,077	1,063		1,066	v (C–O–C)
869	880	869	897	887	v (C–H), aromatic ring

^{1}H-NMR spectrum of all the three block copolymers. For [NR/PU]-1 (Fig. 2c) the peak assignments for NR soft segment protons are at 2.4 ppm (H_1), 4.94 ppm (H_2), 1.56 ppm (H_3) and that of PU protons are at 4.31 ppm (H_4), 1.2 ppm (H_{11}), 3.7 ppm (H_9), 2.04 ppm (H_{10}) and a multiplet at around 7.21 ppm (H_7). Peaks observed at 2.27 ppm (H_1), 5.76 ppm (H_2), 2.02 ppm (H_3) (Fig. 2d) and 1.67 ppm (H_1), 5.12 ppm (H_2), 2.04 ppm (H_3) (Fig. 2e) are the NR soft segment protons of [NR/PU]-2 and [NR/PU]-3 block copolymers, respectively. PU hard segment resonances of [NR/PU]-2 occur at 4.57 ppm (H_4), 1.22 ppm (H_9), 3.33 ppm (H_{10}) and a multiplet at around 7.97 ppm (H_7). Similarly, those for [NR/PU]-3 occur at 4.44 ppm (H_4), 1.5 ppm (H_{12}), 3.88 ppm (H_9), 2.84 ppm (H_{12}) and a multiplet at around 7.99 ppm (H_7). ^{13}C spectrum also consists of the soft segment and hard segment transitions (Fig. 3a–c). These assignments reveal that the spectrum contains all the characteristics of the NR soft segment and the PU hard segments, which are enough to characterise the block copolymer. The NMR spectra of all the samples clearly indicate the chain extension of NR with the respective hard segments.

On the basis of spectroscopic analysis, the course of the reaction and the final products are shown in Scheme 2.

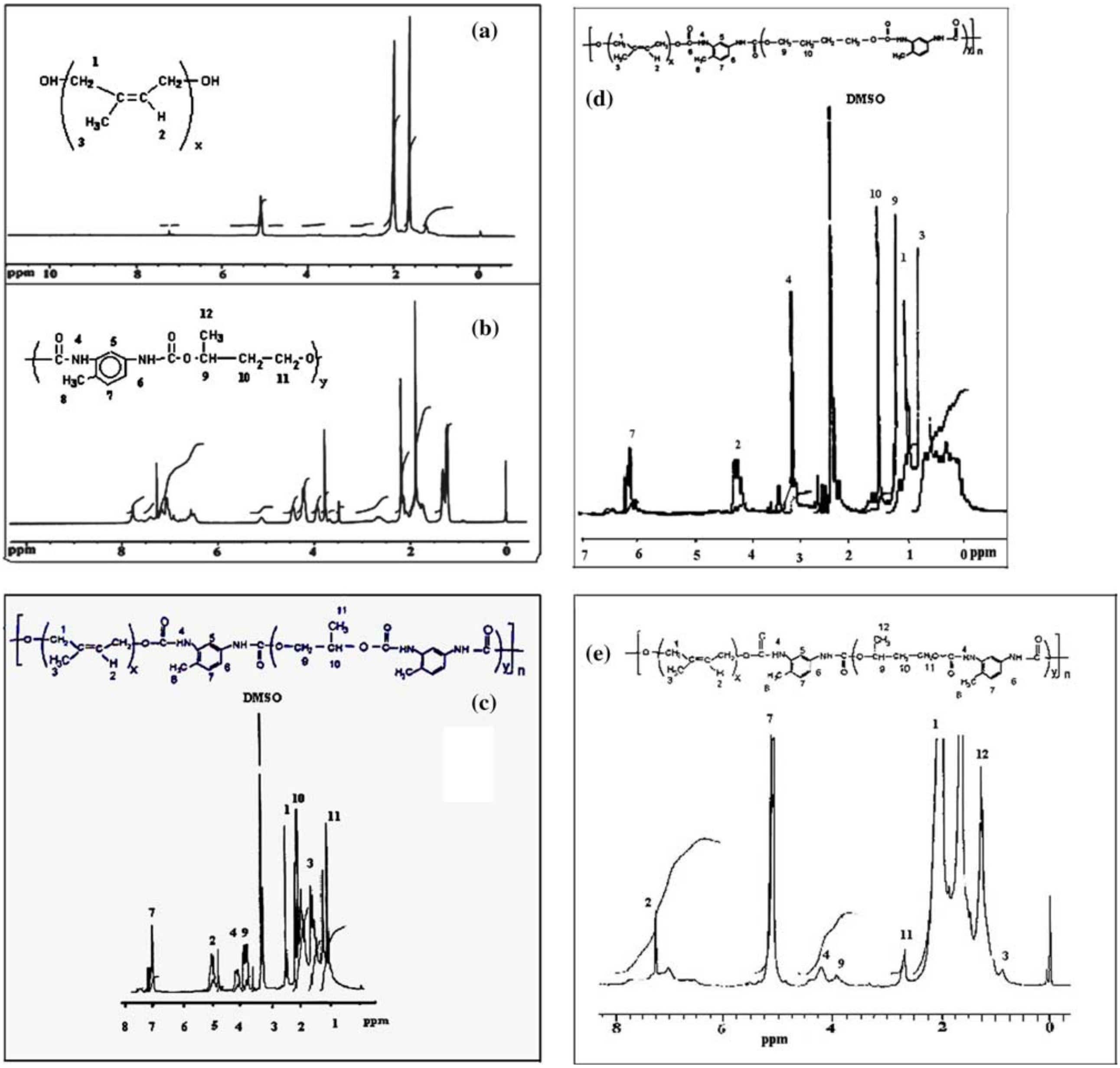


Fig. 2 ^{1}H-NMR spectrum of (**a**) HTNR, (**b**) PU hard segment of [NR/PU]-3, (**c**) [NR/PU]-1, (**d**) [NR/PU]-2 and (**e**) [NR/PU]-3 block copolymers

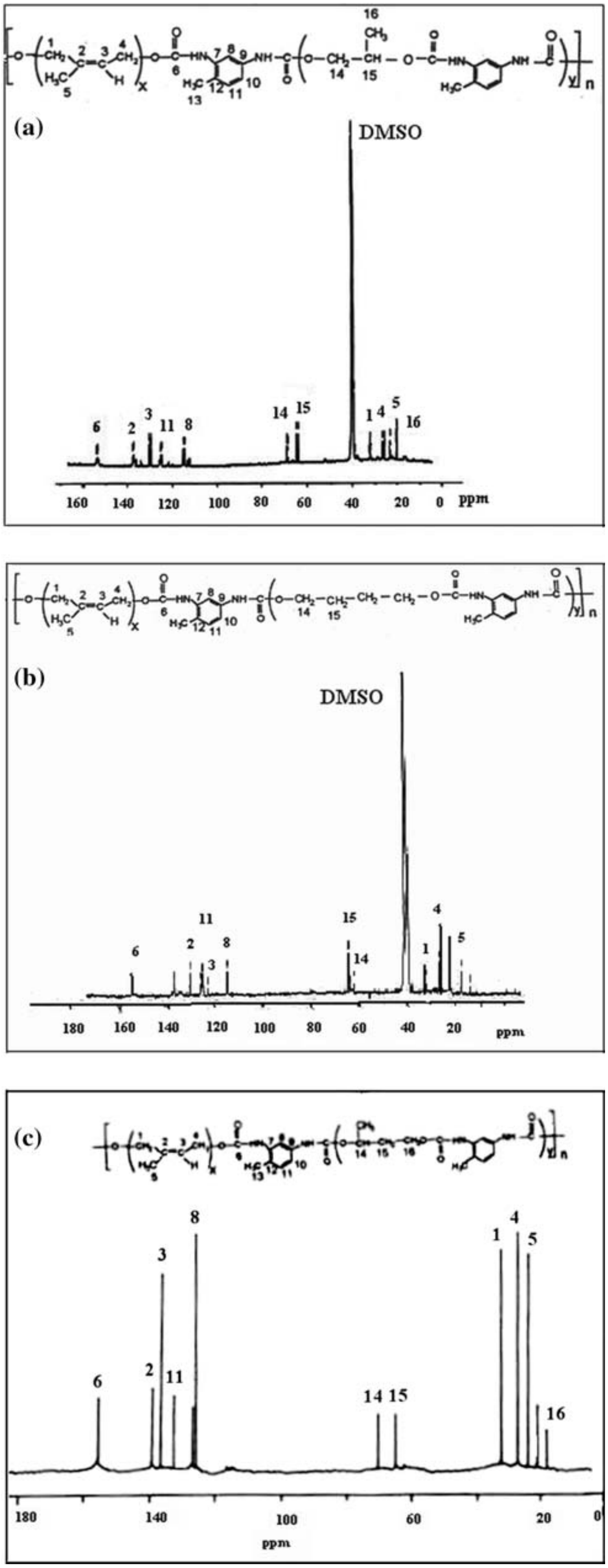
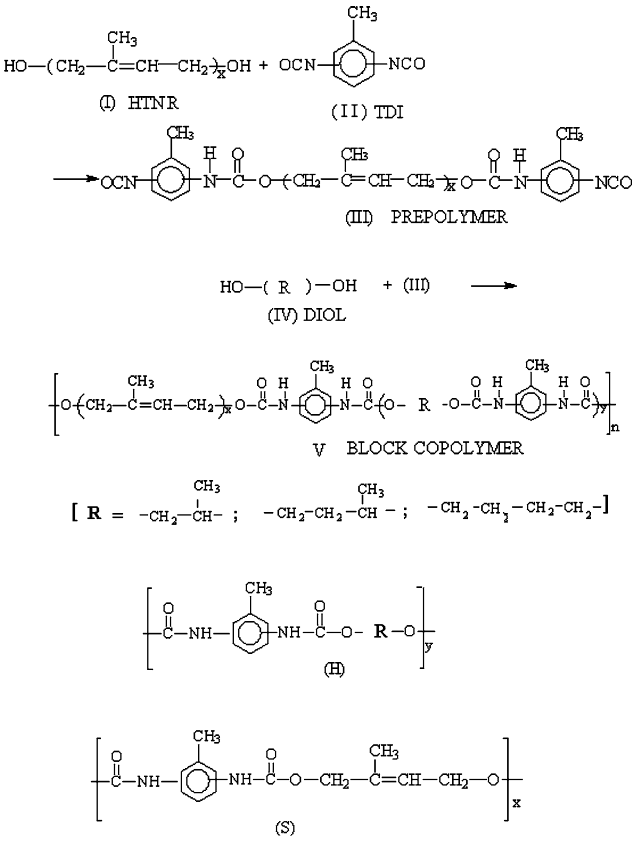


Fig. 3 ^{13}C-NMR spectrum of (**a**) [NR/PU]-1, (**b**) [NR/PU]-2 and (**c**) [NR/PU]-3 block copolymers



Scheme 2 Course of the block copolymerisation reaction and the structure of the block copolymer (H), hard segment; (S), soft segment

GPC analysis

All the three samples were analysed by gel permeation chromatography and the data tabulated in Table 3. GPC traces showed that all the samples contain only a single fraction with moderate level of molecular weight distribution. The molecular weight values indicate that the products are low molecular weight polymers.

Solution viscosity measurements

Ubbelohde viscometer was used to find out the flow time values for the test solutions. The intrinsic viscosity [η], values are found to be 0.2603, 0.2752 and 0.2656 dl/g for

Table 3 Dilute solution viscosity values and molecular weights of the block copolymers from GPC

Sample	[η] (dl/g)	$\overline{M}_n$	$\overline{M}_w$	Dispersity
(NR/PU)-1	0.2603	14,000	31,400	2.242
(NR/PU)-2	0.2752	14,877	33,640	2.261
(NR/PU)-3	0.2656	14,113	31,810	2.253

(NR/PU)-1, (NR/PU)-2 and (NR/PU)-3, respectively. Using the GPC value of molecular masses, solving the Huggins equation for two pairs of the block copolymers, average '*K*' and '*a*' values are computed [29]. The average values of *K* and a computed in the present case are 2.88×10^{-2} dl/g and 0.7536, respectively. Generally, the value of '*a*' is found to be in the range 0.5–0.8, and Kin the range 10^{-3} to 10^{-1} for flexible chains. This comes true in the present case, in which all the block copolymers are highly flexible elastomers.

DSC analysis

The DSC analysis was carried out on all the samples and the data are given in Table 4. The DSC curve (Fig. 4a) of [NR/PU]-1 shows two thermal transitions. The first sub ambient transition at –58°C is a glass transition (T_g), and it corresponds to that of NR soft segment of the block copolymer, which is close to that of HTNR (–60°C). At 72.09°C, another T_g is observed, which is attributed to the transition of the polyurethane phase in the block copolymer. This is in the expected range and is caused by the high intermolecular forces present in polyurethane blocks such as hydrogen bonding between the >NH and >CO groups of polyurethane blocks of neighbouring chains. Besides, the intervening aromatic rings due to TDI in the molecular structure reduce chain mobility, rendering the polyurethane chains highly rigid, which soften only at higher temperatures.

Table 4 T_g values and the transition temperatures for the NR/PU block copolymers

Sample	T_g of the soft segment (°C)	T_g of the hard segment (°C)	Degradation cum melting endotherm, T_m (°C)
(NR/PU)-1	–58.0	72.09	185
(NR/PU)-2	–59.0	76.41	198
(NR/PU)-3	–56.5	68.76	192

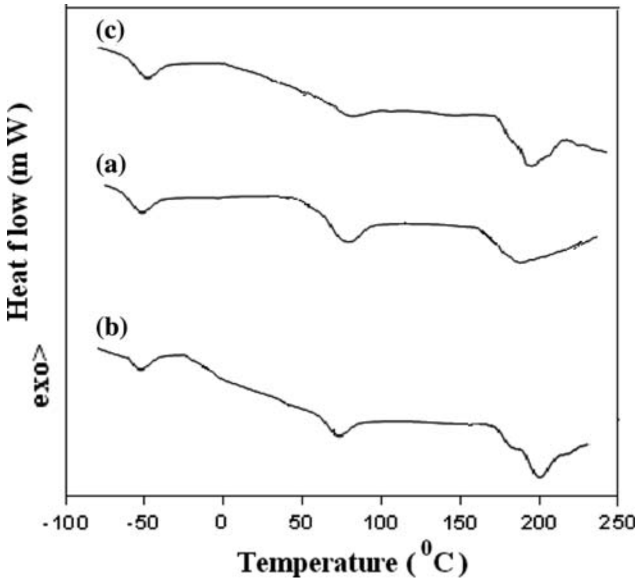


Fig. 4 DSC thermograms of NR/PU block copolymers (**a**) [NR/PU]-1, (**b**) [NR/PU]-2 and (**c**) [NR/PU]-3

Above the T_g of polyurethane, the thermogram shows a very prominent endotherm at 185°C. The polyurethane phase also overcomes the restricted mobility above T_g viz., 72°C in the case of this sample. This is promoted by the linear chain structure of the polyurethane segments. The long-range order thus established would collapse at still higher temperature and the endotherm observed at the peak temperature of 185°C is expected to be the melting temperature. Hence, it is to be concluded that the polyurethane segments undergo decomposition along with the melting transition.

The DSC thermograms (Fig. 4b and c) of the other two samples, viz., [NR/PU]-2 and [NR/PU]-3 show the same pattern as [NR/PU]-1. The subambient T_g due to NR segment is at –59°C for the former and –56.5°C for the latter. However, the T_g corresponding to the polyurethane phase occurs at different temperatures, i.e. 76.41 and 68.76°C, respectively (Table 4). The peak temperatures of the subsequent endotherm, attributed to melting with endothermic degradation remain almost unchanged in all three samples, which shows that the hard segment length does not cause variation in these values. Since these three samples are synthesised in very nearly equimolar NCO and OH concentrations, allophanate formation is not expected and hence, the second transition could be a melting endotherm of the linear PU segments.

Comparative study of the DSC data of block copolymers shows that they are made up of two different phases, as indicated by the transitions at –59° to –56.5°C and another around 70°C, which shows that phase separation in the samples is nearly complete. T_g of the hard segment varies with the extender diol in the order 1,4-BDO > PG > 1,3-BDO. The polyurethanes with the above diols show T_g of 76.41, 72.09 and 68.76°C, respectively. This trend determines the extent of flexibility of polyurethane chain formed from TDI and the respective diol, which is governed by factors such as hydrogen bonding, bulky groups, etc. In 1,4-BDO based block copolymer, the linear carbon chain introduces some extent of uniformity to the polyurethane segments, which would lead to chain alignment, restricting the flexibility of polyurethane chain showing the maximum value. Next in the order is PG based sample, the protruding methyl group in the diol part of the polyurethane chain causes increased spacing between neighbouring segments, thus diminishing intermolecular attraction with further increase in flexibility, and T_g becomes lower than the former block copolymers. Regarding the 1,3-BDO sample, the diol part consists of a three carbon chain with a protruding methyl group, which hinders the chain alignment and thus reduces chain stiffness compared to the diol part in 1,4-BDO and PG based samples. This explains the lower T_g of NR/1,3-BDO compared to 1,4-BDO. In short, the hard segment transition in the above block copolymers are the manifestation of the chain flexibility, which in turn is determined by the diol structure in the polyurethane repeat unit with the diisocyanate common to all. The lower T_m of this series of copolymers is attributed to the formation of linear structure and hence, it shows solubility with lower mechanical properties. The linear samples will have more free chain end segments than a cross-linked high molecular weight sample. The larger the number of chain end segments, the larger will be the effective segmental motion [30]. Thus, the T_g value will be lower for linear polymers.

Tensile properties

Present samples show low tensile properties as shown in Fig. 5. However, the highest value of tensile strength and modulus of elasticity is seen in the case of (NR/PU)-3. A common trend observed in the tensile behaviour of all the samples is that they undergo a large initial elastic deformation and at the end of this deformation, the curve enters a yield region and stops. The initial elastic elongation is due to the NR component in the sample, which is present as the major part, i.e. 70%. This is the more flexible part and hence undergoes initial deformation. Yield region observed in the latter part of the tensile curve is attributed to the plastic component in the block copolymers. This kind of tensile behaviour is new for the present block copolymer systems and not observed previously for samples prepared by the previous synthetic method. In that case, yield occurs early during the deformation followed by a large elastic elongation and failure. The present samples seem to show an appropriate tensile behaviour characteristic of a block copolymer of TPE type. This could be an advantage derived from the present modified synthetic method that is likely to offer a more perfect block copolymer structure.

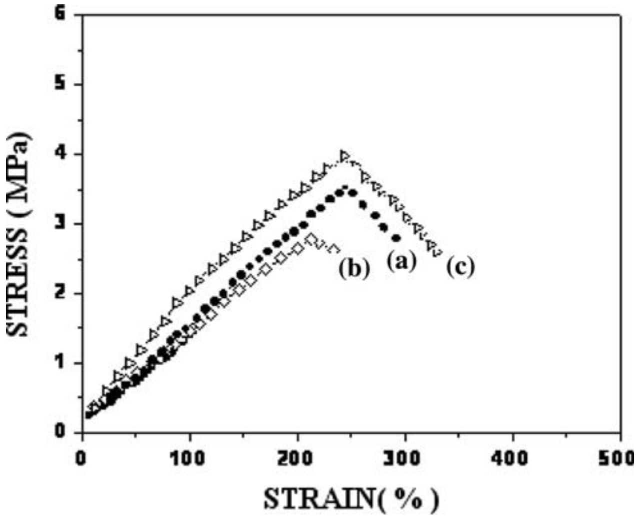


Fig. 5 Stress–strain curves of [NR/PU] block copolymers; (**a**) [NR/PU]-1, (**b**) [NR/PU]-2 and (**c**) [NR/PU]-3

SEM analysis

The fracture surfaces of the copolymers viz., (NR/PU)-1, (NR/PU)-2, (NR/PU)-3 were investigated by SEM. Figure 6a–c shows the SEM micrographs with same magnification 1,000× of (NR/PU)-1, (NR/PU)-2 and (NR/PU)-3, respectively. The micrographs shows continuous rubber matrix, in which the hard domains are randomly distributed with diffused domain boundaries. In the present case, it was not possible to locate hard domains of PU characteristic of a block copolymer dispersed in the bulk. The absence of hard domains on the surface may be caused by the low hard segment content. A possible explanation was given by Chen-Sai et al. [31] that the domains are so dilute and the inner potential difference between the two phases is so small that the contrast is too low. Due to the extreme small size; it would not be visible under this study.

Conclusions

Syntheses of soluble block copolymers were achieved by optimising the reaction conditions and keeping low NCO/OH ratio. Molecular weight values of the samples, determined by GPC, suggested that they are low molecular weight polymers. IR and NMR studies showed that these block copolymers are phase separated systems containing an NR soft segment and a PU hard segment. DSC studies indicated three thermal transitions; soft segment transition around –59°C, hard segment transition in the 70–75°C range, depending on the structure of the chain extender diol and degradation cum melting transition around 200°C. Since these three samples are synthesised in very nearly equimolar NCO and OH concentrations, allophanate formation is not expected. Low T_g values, inferior mechanical properties, etc. are manifestations of chain flexibility of these block copolymers. The lower T_m of this series of copolymers is attributed to the formation of linear structure and hence, it shows solubility with lower mechanical

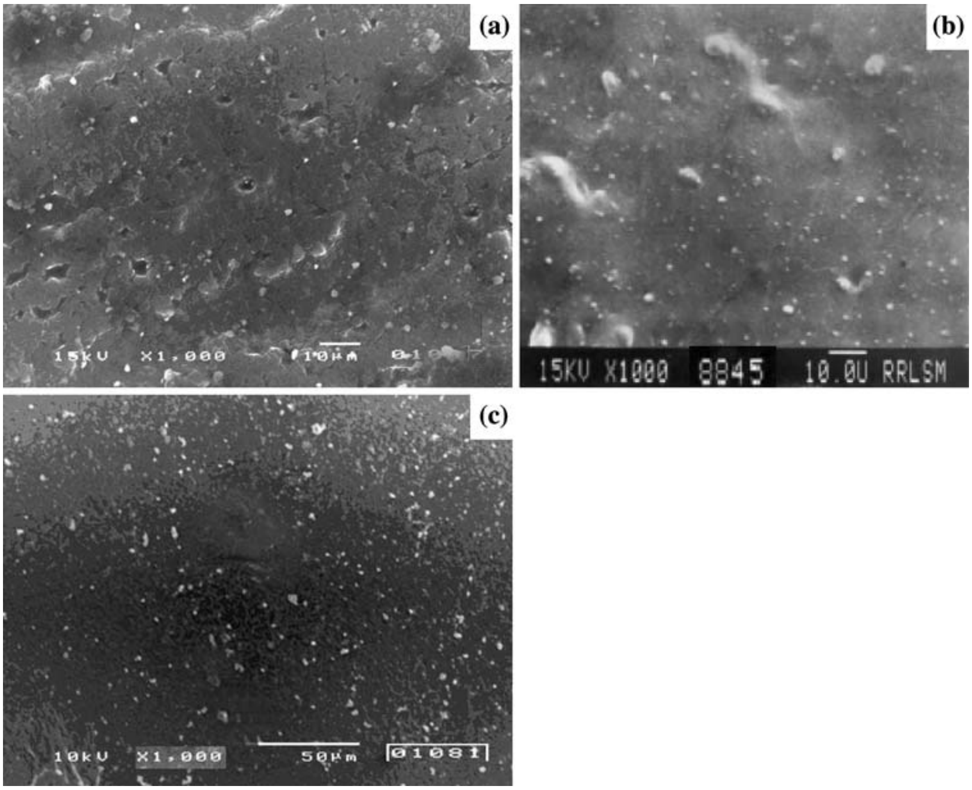


Fig. 6 SEM micrographs of [NR/PU] block copolymers; (**a**) [NR/PU]-1, (**b**) [NR/PU]-2 and (**c**) [NR/PU]-3

properties. SEM analysis showed continuous rubber matrix, in which the hard domains are randomly distributed with diffused domain boundaries.

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