

Synthesis and Thermal Studies of Block Copolymers from NR and MDI-Based Polyurethanes

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ABSTRACT: Five series of block copolymers based on natural rubber and polyurethane were prepared from hydroxyl terminated liquid natural rubber (HTNR) and polyurethane (PU) formed by the reaction of diphenyl methane—4,4'—diisocyanate (MDI) with a chain extender diol, viz., ethylene glycol (EG)/propylene glycol (PG)/1,4-butane diol (1,4-BDO)/1,3-butane diol (1,3-BDO)/bisphenol A (BPA), by solution polymerization. Structural characterization of the block copolymers was done by infrared (IR) analysis. Thermal studies and kinetic analysis on thermal degradation of the block copolymers were undertaken with the view of characterizing them. Energy of activation and entropy change for the degradation were determined

and a probable mechanism for the solid state degradation was suggested which corresponds to a three dimensional diffusion mechanism. DSC analysis has been used for the study of microphase separation in the block copolymers. Thermal transition of the hard segment significantly varies with the extender diol which highlights the effect of extender diol structure on the chain stiffening mechanism. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 19–28, 2009

Key words: polyurethane; block copolymer; natural rubber; differential scanning calorimetry; thermogravimetric analysis

INTRODUCTION

Block copolymers with heterophase morphology are the best candidates for studying structure—property relation existing in them. Heterophase morphology in this class of materials is observed as microphase separation that has been extensively studied by many authors.^{1–3} A wide range of properties is possible for these block copolymers which is attributed to the respective degree of microphase separation.^{4,5} However, it has been argued that a certain level of phase mixing is also necessary for the polymers to exhibit improved properties.⁶ All these aspects depend on the chemical constitution of the component polymers. The conventional polyurethane elastomers with polyester/polyether soft segments and polyurethane hard segments show higher properties since both the blocks involve in intermolecular interactions which obviously lead to interphase mixing.^{7,8} On the other hand block copolymers derived from nonpolar polydiene soft segment and polar hard segment give completely phase separated systems.^{9,7} However, their properties seem to be slightly inferior to the polyurethane

elastomers. This must be due to the absence of phase interaction.¹⁰ Block copolymers based on polyisobutylene,¹⁰ polybutadiene,¹¹ polydimethyl siloxane¹² and polymyrcene¹³ are well-known examples for this category of materials. Studies on these block copolymers revealed that microphase separation in block copolymers is influenced by factors such as differential solubility parameter, segment length, crystallinity of either segment, compositional heterogeneity of the segments, intermolecular interactions etc. Superior hydrolytic stability, higher oxidative stability, improved low temperature flexibility and variations in gas permeability are certain advantages of this type of materials. Recent example to this category of block copolymers are those based on liquid natural rubber and polyurethane oligomers.^{14–16} The latter constituent is the hard phase and it has been derived from a dissymmetric diisocyanate, viz., 2,4—toluene diisocyanate on reaction with a chain extender diol such as propylene glycol, 1,3-butane diol or bisphenol A. However, it is interesting to follow the effect of symmetric diisocyanate such as MDI (4,4'-diphenyl methane diisocyanate) on the properties of this group of block copolymers. Present work focuses on the synthesis and thermal characterization of a few series of such block copolymers. The information gathered from the thermal data is used to probe the temperature induced changes in polyurethane microdomains. Besides, the TGA data have been used in studying the degradation kinetics.

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EXPERIMENTAL

Materials

Natural crumb rubber (ISNR-5) with weight average molecular weight 820,000, intrinsic viscosity in benzene at 30°C = 4.45 dL/g and Wallace Plasticity, $\rho^\circ = 39.0$ was supplied by Rubber Research Institute of India, Kottayam. Hydrogen peroxide (30% aqueous solution, E. Merck, India) was used as such. Toluene (reagent grade, E. Merck, India) and methanol (E. Merck, India) were used without further purification. Diphenyl methane-4, 4'-diisocyanate (MDI, synthesis grade, Merck, Germany) was used as such without further purification. Ethylene glycol (E. Merck, India), propylene glycol (E. Merck, India) and 1, 3-butane diol (1,3-BDO, Merck, Germany) were dried with anhydrous calcium oxide and then distilled under reduced pressure. Bisphenol A (BPA, Merck, Germany) was fused and dried in vacuum before use. Dibutyl tin dilaurate (DBTDL, Fluka, Switzerland) was used without further purification. Tetrahydrofuran (THF, reagent grade, BDH, India) was dried by sodium wire and distilled before use. Chloroform (synthesis grade, E. Merck, India) was used after distillation.

Hydroxyl terminated liquid natural rubber (HTNR) of number average molecular weight 4500 was prepared in our laboratory by the photochemical degradation of natural rubber as per reported procedure.¹⁷ It was reprecipitated twice from toluene using methanol and dried at 70–80°C in vacuum.

Synthesis of block copolymers

The synthesis was carried out by the two-shot process.^{14–16} Required stoichiometric amount of HTNR (Table I) was dissolved in chloroform (25% w/v), DBTDL catalyst, quantity of which was noted in a later section, viz., "Copolymer synthesis", was added and the solution was brought to reflux at 60–65°C. The final stoichiometric amount of MDI in chloroform (25% w/v) was dropped into it over a period of 30 min, followed by one and a half hour reaction to endcap the HTNR. The required amount of chain extender diol in chloroform (25% w/v) was then added and stirring continued until the reaction mixture became very viscous (≈ 25 min to 1.5 h). The product was then cast on a glass plate coated with silicon release agent, removed and cured at 65°C followed by two weeks ageing at room temperature.

Polymer designation

The samples of block copolymers prepared have been designated as follows. As an example, NR/EG (70/30) means that the sample contains about 70% by weight of natural rubber (NR) and about 30% by

TABLE I
Molar Composition of Reactants in the NR/PU Block Copolymers

Sample	Molar composition HTNR/MDI/DIOL
NR/EG(70/30)	1.0/07.17/06.17
NR/EG(60/40)	1.0/10.60/09.60
NR/EG(50/50)	1.0/15.41/14.41
NR/EG(40/60)	1.0/22.61/21.61
NR/EG(30/70)	1.0/34.63/33.62
NR/PG(70/30)	1.0/06.91/05.91
NR/PG(60/40)	1.0/10.19/09.19
NR/PG(50/50)	1.0/14.79/13.79
NR/PG(40/60)	1.0/21.69/20.68
NR/PG(30/70)	1.0/33.18/32.18
NR/BDO ^a (70/30)	1.0/06.66/05.66
NR/BDO(60/40)	1.0/09.81/08.81
NR/BDO(50/50)	1.0/14.22/13.22
NR/BDO(40/60)	1.0/20.83/19.83
NR/BDO(30/70)	1.0/31.85/30.85
NR/BPA(70/30)	1.0/05.03/04.03
NR/BPA(60/40)	1.0/07.27/06.27
NR/BPA(50/50)	1.0/10.40/09.40
NR/BPA(40/60)	1.0/15.11/14.11
NR/BPA(30/70)	1.0/22.95/21.95

^a BDO: 1,3-BDO and 1,4-BDO.

weight of polyurethane based on ethylene glycol and biphenyl methane—4,4'—diisocyanate.

The overall composition for the synthesis of various block copolymers was calculated in molar ratios of the respective reactants. For example, the overall composition for the synthesis of NR/EG (70/30) is 1.0/7.17/6.17 which is the ratio of the number of moles of HTNR, MDI, and EG. The above ratio was calculated as follows on the assumption that the reaction between EG and MDI is fast and instantaneous under the given reaction conditions.

The number average molecular weight of HTNR was determined by gel permeation chromatography to be 4500. Molecular mass of polyurethane required for NR/EG(70/30) is $(30/70) \times 4500 = 1928.5$. This mass of PU is constituted by $1928.5 \times 62 / (62 + 250.21) = 382.96$ g or 6.17 mol of EG and $1928.5 \times 250.21 / (62 + 250.21) = 1545.53$ g or 6.17 mol of MDI, where 62 and 250.21 are the molecular weight of EG and MDI, respectively. Thus it becomes an equimolar reaction which 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 one mole less MDI, i.e., 5.17. This would yield hydroxyl terminated PU chains of the required molecular weight. An additional 2 mol of MDI were required to endcap HTNR with isocyanate groups. Thus the total number of moles of MDI required = $5.17 + 2 = 7.17$ mol = 1794.00 g Now the weight percentage of hard segment (PU) = $[(1794.00 + 382.54) / (1794.00 + 382.54 + 4500)] \times 100 = 32.6\%$. An excess of 5% of MDI (equal to 0.36 mol) was added to compensate any loss during

transfer and side reactions. Similar calculation was adopted for other compositions as well.

The weight percentage of the PU content obtained in the above calculation is kept constant for all series involving the different extender diols by varying the molar composition of the reactants as in Table I. Thus, the calculated values of the polyurethane content of different samples in each series of the block copolymers work out to be 32.60, 41.94, 51.37, 60.86, and 70.49%, respectively, for the NR/PU(70/30), NR/PU(60/40), NR/PU(50/50), NR/PU(40/60), and NR/PU(30/70). PU stands for the polyurethanes formed from the respective extender diol and the diisocyanate.

Measurements

Thermogravimetric analysis

The thermal stability of the block copolymer was followed by using a Delta series TGA 7 Analyser at a scanning rate of 10°C/min in nitrogen atmosphere. Samples were scanned from 30°C -750°C.

Differential scanning calorimetric analysis

The thermal behavior of the block copolymers was studied by DSC on a Mettler Thermal Analyser equipped with a liquid nitrogen subambient cooling accessory at a heating rate of 10°C/min and a sensitivity of 5 m cal⁻¹. Mass of the sample was ~ 10 mg. All DSC scans were in -100 to 300°C range and were first scans.

RESULTS AND DISCUSSION

Copolymer synthesis

The synthesis of the block copolymers was carried out according to reported procedure.¹⁴⁻¹⁶ The two types of segments, viz., the NR and polyurethane are termed as the soft and hard segments, respectively. NR behaves as the soft segment due to its inherent flexibility. Since the polyurethanes are very rigid, they form the hard segments. The synthesis has been carried out in five series based on the type of chain extender used, viz., EG, PG, 1,3-BDO, 1,4-BDO and BPA. Required stoichiometric amounts of HTNR and the chain extender diol used in the synthesis are given in Table I. The amount of DBTDL catalyst added in the preparation of each series of the block copolymer varies with the type of extender diol used and it was fixed in each case by a trial and error method. It is 0.1% (w/v) with respect to the weight of HTNR for EG and 1, 4-BDO series which is increased to 0.2% (w/v) for PG and 1,3-BDO series. Still higher quantity of 0.3% (w/v) was used for BPA series. This suggests that there is variation in

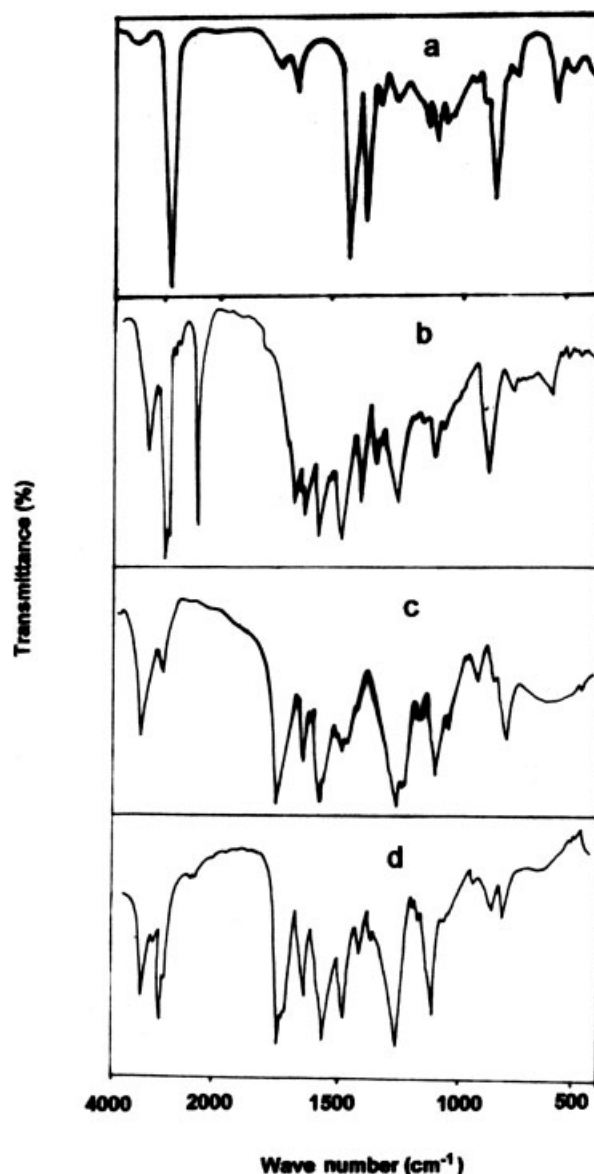
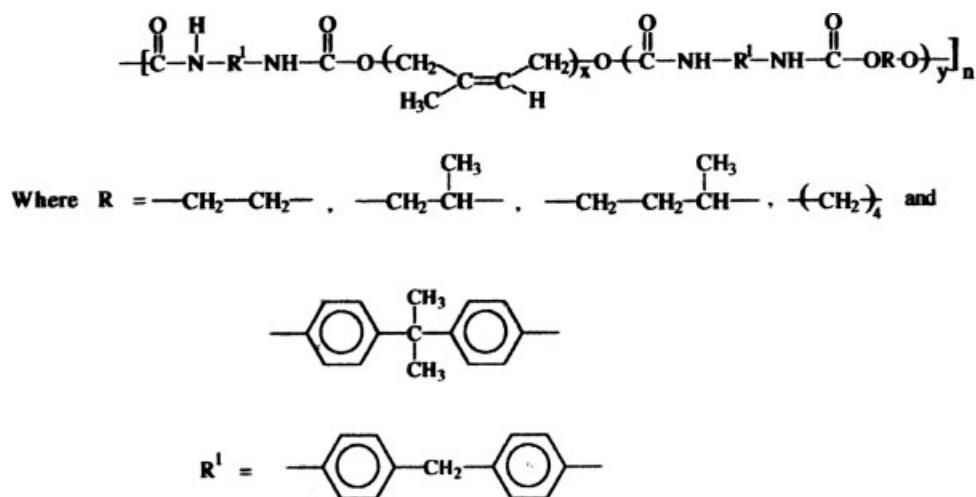


Figure 1 IR spectrum showing the course of block copolymerisation of NR/EG (50/50): (a) HTNR, (b) NCO endcapped HTNR, (c) MDI/EG polyurethane and (d) NR/EG (50/50).

the reactivity of the chain extender diol with MDI. In the case of ethylene glycol and 1, 4-butane diol, which have primary hydroxyl groups, the reaction is faster in the presence of lower amount of DBTDL. But for the propylene glycol and 1,3-butane diol endowed with secondary hydroxyl group as well, the reaction becomes slower and therefore higher quantity of the catalyst was required. The effect of phenyl group present in the extender diol on the reactivity is seen for BPA-based synthesis. In the case of secondary hydroxyl groups, the steric crowding around the hydroxyl bearing carbon creates difficulty in easy approach to the carbon of the isocyanate group during the nucleophilic addition across



Scheme 1 Structure of NR/PU block copolymers.

the ---N=C--- group according to the mechanism proposed.¹⁸

Characterization of the product

Infrared spectroscopic analysis has been used for following the course of block copolymerisation and to establish the structural identity of the products. The IR studies have been carried out by focusing on three principal regions, viz., ---OH stretching ($3600\text{---}3400\text{ cm}^{-1}$), ---NH stretching ($3500\text{---}3200\text{ cm}^{-1}$) and the >C=O stretching (1700 cm^{-1}) since changes occur only to these bands during the block copolymerization reaction. These absorption bands are common for all the samples of the five series, irrespective of the chain extender and the composition and hence only a representative sample, viz., NR/EG (50/50) has been described here.

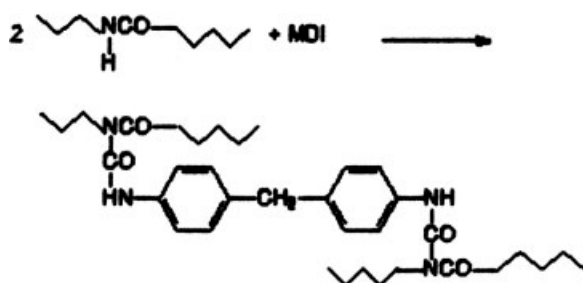
Progressive changes occurring during the block copolymerization reactions have been followed by analyzing the reaction mixture, withdrawn from the reaction kettle. The final product in the form of a thin film was subjected to etching process successively with toluene and dimethyl formamide to remove unreacted liquid NR and the polyurethane before taking the spectrum.

The spectra taken during the two-shot block copolymerization of the above sample are depicted in Figure 1. Spectra given in the figure include those of (a) HTNR, (b) the ---NCO endcapped HTNR, (c) polyurethane (PU) oligomer formed from diphenyl methane diisocyanate (MDI) and ethylene glycol and (d) the block copolymer formed. A comparison of the spectra of HTNR [Fig. 1(a)] and the ---NCO endcapped HTNR shows that the bands at $3600\text{---}3400\text{ cm}^{-1}$ due to hydroxyl groups disappeared and new bands at 3300 cm^{-1} , 1703 cm^{-1} , and 2200 cm^{-1} appeared during the endcapping process. This indi-

cates that the reaction between hydroxyl group and the isocyanate group has been successful to form urethane group which gives >NH band at 3300 cm^{-1} , >C=O band at 1703 cm^{-1} and the ---NCO band at 2260 cm^{-1} . To this system the chain extender diol, viz., EG was added to get the final product. The final product shows the disappearance of ---NCO band at 2260 cm^{-1} and at the same time the intensity of the >NH and the >C=O band has increased to a greater extent. Moreover it shows all the absorption bands due to the constituent polymers, viz., liquid NR and the PU oligomers. The characteristic IR spectra of NR/EG comprises of the following peaks: 3300 cm^{-1} (---NH stretching), 2930 cm^{-1} (---CH_2 asymmetric stretching), 2860 cm^{-1} (---CH_2 symmetric stretching), 1703 cm^{-1} (hydrogen bonded >C=O stretching), 1595 cm^{-1} (aromatic C=C stretching) and 1220 cm^{-1} (in plane bending of >CH_2) [Fig. 1(d)]. All these changes indicate the successful chain extension reaction between the ---NCO endcapped HTNR and the polyurethane segments to form a block copolymer whose structure is shown in Scheme 1.

Although this scheme indicates the structure of the repeat unit in the polymer chain the polymer seems to possess a low degree of crosslinking as observed by its insolubility but a high extent of swelling in solvents like tetrahydrofuran. This factor makes the determination of molecular weight impossible. The crosslinking is explained on the basis of allophanate formation as shown in Scheme 2. Swelling study was also carried out on these samples which form the theme of a subsequent publication.

Identical molecular characteristics among the block copolymers in a given series and also in the different series are maintained by controlling the molar proportion of the constituents. For example, the hard segment length is determined by the proportion of



Scheme 2 Formation of allophanate linkage in block copolymers.

the diol and diisocyanate which is varied uniformly in all the five series. The level of chain extension of NR with polyurethane segment would depend on the molar quantity of diisocyanate which is also maintained uniformly in all the series.

Thermal characteristics

Differential scanning calorimetric analysis

The DSC analysis was carried out only on selected samples in each series, viz., 70/30, 50/50, and 30/70 compositions since the samples in a given series are expected to show similar features. For the same reason only the DSC curves of representative samples are shown in Figure 2. However, the data of all compositions analyzed are given in Table II. The thermogram of NR/EG (70/30) shows four thermal transitions. The first subambient transition at -64°C is a glass transition (T_g) and it corresponds to that of NR. At 91.4°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 it is caused by the high intermolecular forces present in polyurethane blocks such as hydrogen bonding between the $>\text{NH}$ and $>\text{CO}$ groups of polyurethane blocks of neighboring chains. Besides, the intervening aromatic rings due to MDI in the molecular structure reduce chain mobility, rendering the polyurethane chains highly rigid which soften only at higher temperatures.

Above the T_g of polyurethane, the thermogram shows a very prominent exotherm at 190°C , followed by a strong endotherm with a peak temperature at 260°C . This feature is characteristic of a crystallisable polymer, wherein the polymer segments suffers from restricted mobility and may not be in thermodynamic equilibrium as a result of rapid setting of the viscous sample after casting, thereby not reaching their equilibrium conformation. This inherent non equilibrium nature of the amorphous phase undergoes a transition, during DSC analysis, leading to the attainment of equilibrium state by packing and conformational change, which causes enthalpy

relaxation and an exothermic peak at 190°C . Besides, the polyurethane phase also overcomes the restricted mobility above 90°C . Thus the segments of PU phase move into crystallites, contributing towards the exotherm. 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

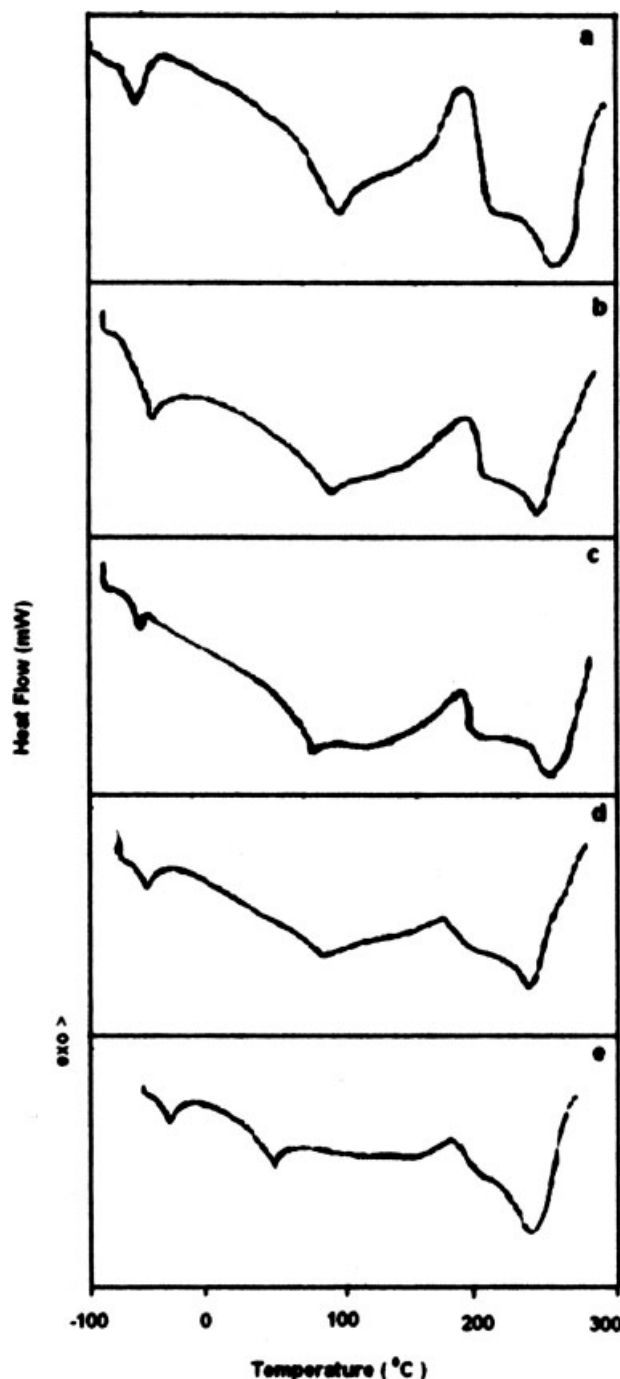


Figure 2 DSC thermograms of NR/EG block copolymers: (a) NR/EG(70/30), (b) NR/PG(70/30), (c) NR/1,3-BDO(70/30), (d) NR/1,4-BDO(70/30), and (e) NR/BPA(70/30).

TABLE II
DSC Results of the NR/PU Block Copolymers

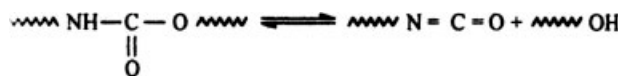
Sample designation	T_g of NR phase ($^{\circ}\text{C}$)	Transitions in polyurethane phase		
		T_g ($^{\circ}\text{C}$)	Crystallisation temp ($^{\circ}\text{C}$)	Melting cum degradation temp ($^{\circ}\text{C}$)
NR/EG (70/30)	-64.0	91.4	190.0	260.0
NR/EG(50/50)	-64.0	103.3	191.6	263.3
NR/EG(30/70)	-62.0	106.5	188.2	261.4
NR/PG(70/30)	-64.0	88.0	194.9	249.8
NR/PG(50/50)	-60.0	96.0	194.9	251.3
NR/PG(30/70)	-60.0	99.9	190.0	248.0
NR/1,3-BDO(70/30)	-62.0	76.6	193.2	263.2
NR/1,3-BDO(50/50)	-60.0	83.2	191.6	278.0
NR/1,3-BDO(30/70)	-64.0	84.9	189.9	290.0
NR/1,4-BDO(70/30)	-64.0	80.0	187.0	258.0
NR/1,4BDO(50/50)	-63.2	86.0	183.0	263.0
NR/1,4BDO(30/70)	-64.0	90.0	179.1	265.0
NR/BPA(70/30)	-60.0	95.5	193.0	261.0
NR/BPA(50/50)	-64.2	106.0	190.0	263.0
NR/BPA(40/60)	-64.0	110.5	190.0	260.0

temperature of 260°C is expected to be the melting temperature. However, this peak in the range of $240\text{--}280^{\circ}\text{C}$ is at the same temperature range¹⁹ as that of the polyurethane back reaction shown in Scheme 3. Hence it is to be concluded that the polyurethane segments undergo decomposition along with the melting transition.

The DSC thermograms of the other two samples, viz., NR/EG (50/50) and NR/EG (30/70) show the same pattern as NR/EG (70/30). The subambient T_g due to NR segment is at -64°C for the former and -62°C for the latter. However, the T_g corresponding to the polyurethane phase occurs at different temperatures, i.e., 103.3°C and 106.5°C , respectively, (Table II). An increase in the hard segment content raises the molecular weight of PU segments, which in turn increases the T_g of the PU phase. The peak temperatures of crystallization and the subsequent endotherm, attributed to melting with endothermic degradation remain unchanged in all three samples, which shows that the hard segment length does not cause variation in these values. This is characteristic of crystalline polymers possessing high intermolecular forces. The thermograms of all other series, viz., the NR/PG, NR/1,3-BDO, NR/1,4-BDO and the NR/BPA series show the same thermal behavior as the NR/EG series.

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 -60° to -64.0° and another around 100°C which shows that phase separation in the samples is nearly complete. The hard segment transition temperature increases with polyurethane content. This is due to the increase in molecular weight of hard segment with its content in the block copolymer. T_g of the hard segment varies with the extender diol in

the order $\text{BPA} > \text{EG} \gg \text{PG} \approx \text{1,4-BDO} > \text{1,3-BDO}$. The polyurethanes with the above diols show T_g of 106.5° , 103.3° , 96° , 86° , and 83°C , respectively. This trend determines the extent of flexibility of polyurethane chain formed from MDI and the respective diol, which is governed by factors such as hydrogen bonding, rigid structural units with ring systems, bulky groups etc. The BPA-based polyurethane segment offers the highest stiffness due to the presence of cyclic ring system and the protruding methyl substituent group on the bisphenol unit which causes T_g value to rise. In the EG based polyurethane samples, the diol part of polyurethane is made up of only a two-membered carbon chain with no side groups and thus expected to reduce stiffness of polyurethane segments and a subsequent reduction in T_g . But since the $-\text{CH}_2-\text{CH}_2-$ part is a very short chain, frequency of urethane group would increase causing high intermolecular interaction and thus NR/EG block copolymer shows the next highest T_g value. In NR/PG samples, the protruding methyl group in the diol part of the polyurethane chain causes increased spacing between neighboring segments, thus diminishing intermolecular attraction with further increase in flexibility and T_g becomes lower than the NR/EG block copolymers. Next in the order is NR/1,4-BDO where in the longer linear butyl group decreases the frequency of occurrence of intermolecular hydrogen bonds and the T_g further decreases. However, the linear carbon chain introduces some extent of uniformity to the polyurethane segments which would lead to chain alignment,



Scheme 3 Decomposition of the urethane linkage.

TABLE III
Thermogravimetric Data of NR/PU Block Copolymers

Sample designation	Onset of mass loss (°C)		% of mass loss		Peak temperature from DTG curve (°C)	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR/EG(70/30)	214.4	380.0	26.4	69.4	290.0	406.0
NR/EG(50/50)	237.0	390.0	48.6	44.4	310.0	413.3
NR/EG(30/70)	238.5	392.0	67.1	29.1	313.3	414.6
NR/PG(70/30)	220.0	382.0	27.6	68.1	307.5	389.0
NR/PG(50/50)	248.0	385.0	46.2	44.1	308.0	403.0
NR/PG(30/70)	250.0	390.0	62.3	28.2	311.0	410.0
NR/1,3-BDO(70/30)	215.0	370.0	27.8	66.0	296.7	376.7
NR/1,3-BDO(50/50)	247.1	383.3	45.4	47.3	306.7	410.0
NR/1,3-BDO(30/70)	248.0	388.9	63.9	29.8	308.0	410.0
NR/1,4-BDO(70/30)	210.0	376.0	26.3	67.0	290.0	380.0
NR/1,4-BDO(50/50)	248.0	380.0	44.6	45.6	303.0	392.0
NR/1,4-BDO(30/70)	248.0	383.8	64.2	27.1	300.0	396.0
NR/BPA(70/30)	193.1	370.0	27.1	63.8	260.0	386.7
NR/BPA(50/50)	199.9	376.7	48.6	50.0	267.0	410.0
NR/BPA(40/60)	220.1	390.0	55.0	36.7	277.0	416.6

restricting the flexibility of polyurethane chain. Net effect is slightly lower T_g for the NR/1,4-BDO samples compared to the NR/EG samples. Regarding the NR/1,3-BDO, 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 NR/1,4-BDO. This explains the lower T_g of NR/1,3-BDO compared to NR/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.

Thermogravimetric analysis

All the samples have been subjected to thermogravimetric analysis. The samples in a given series exhibit common thermal characteristics and hence thermogram of only a selected sample from each series has been presented here. However, data for all the samples are given in Table III. Samples show a two stage degradation pattern which indicates two phase morphology.

Figure 3 shows the TGA curves of three samples of varying composition of NR/EG and one sample each of differing composition from the remaining four series of the block copolymers. Percentage of mass loss in each stage (Table III) indicates that the first stage degradation is due to polyurethane phase and second stage is caused by NR phase. For example, the percentage mass loss in the first stage degradation of NR/EG (70/30) is found to be 26.45% and in the second stage it is 69.4%. Both the values correspond to the theoretical value of the constituent segments in the block copolymers. The samples in the other series, viz., those based on PG, 1,3-BDO, 1,4-BDO and BPA also behave in a similar manner.

The degradation temperature of the polyurethane segments increases with the segment length in a given series of samples. Though the bond stability decides the degradation temperature its variation based on segment length is possible within a range considering the intermolecular forces such as hydrogen bonding and dipole-dipole interaction which are very prominent in PU segments.

Onset temperature of mass loss in the first stage remains very close to each other varying in a range of only 20 to 25°C for all the samples based on aliphatic extenders, viz., EG, PG, 1,3-BDO, and 1,4-BDO. But samples containing BPA exhibit much lower onset temperatures for the first stage degradation between 193°C and 220.1°C. The lower onset temperature indicates lower stability of the polyurethane segments bearing the aromatic chain extender diol. Besides, the distinctly lower degradation temperature of the bisphenol A series of block copolymers compared to those of aliphatic series seems to suggest that the aromatic ring system on the BPA has got destabilising effect on urethane linkage. Its electron-withdrawing property makes the urethane linkage less stable and susceptible to breakage at elevated temperatures. The aromatic ring withdraws electron from the O-atom of the C—O—C linkage in the HN—C(O)—O—C— as shown in Scheme 4 making the bond less stable and prone to breakage. This accounts for the lower thermal stability of NR/BPA block copolymers and the lower onset temperature of their first stage degradation.

The soft segment undergoes degradation almost in the same range of temperature irrespective of its percentage content in the block copolymer and also the nature of the chain extender. This suggests that phase interaction between NR and polyurethane is practically absent in the block copolymers indicating

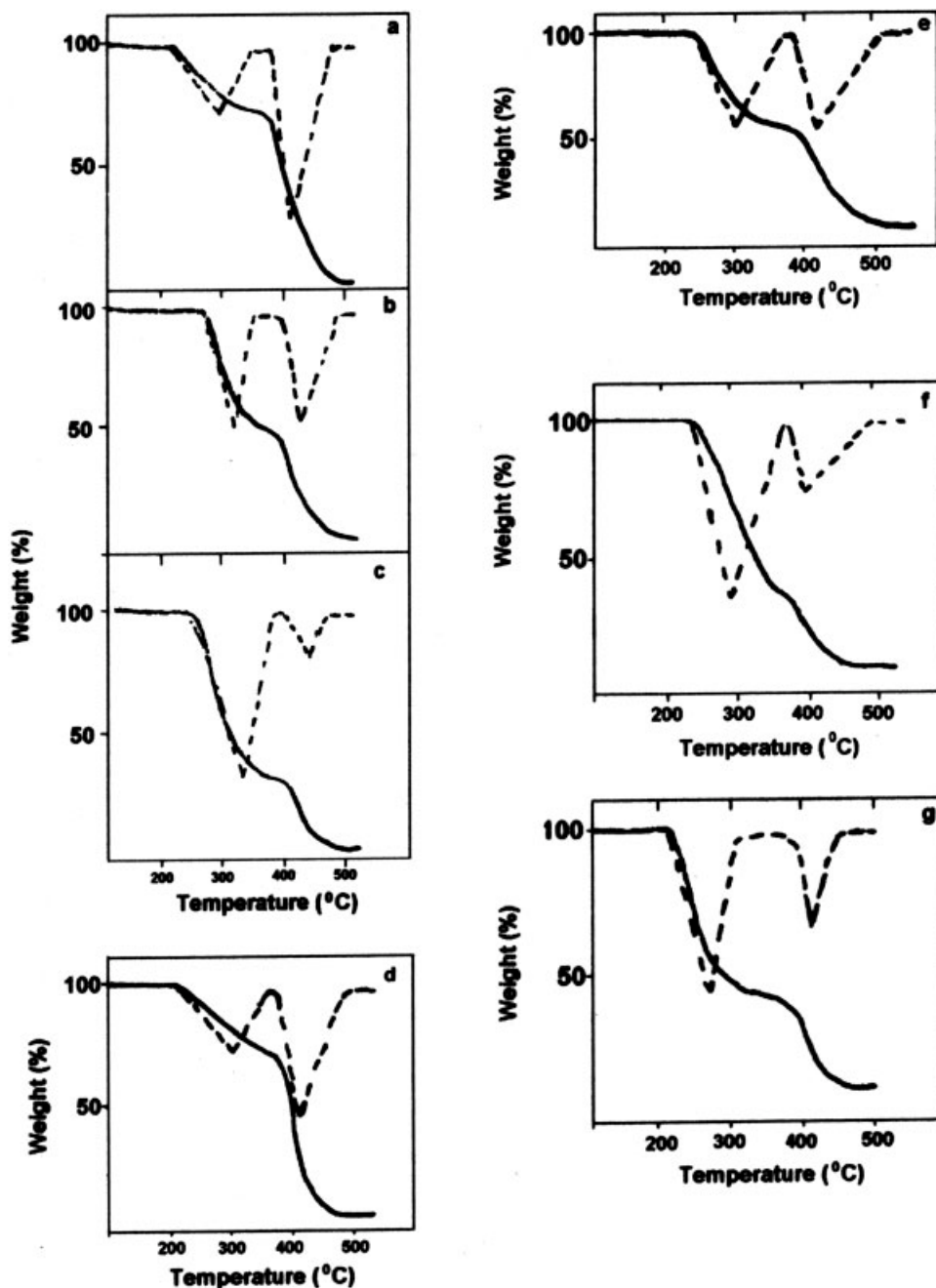
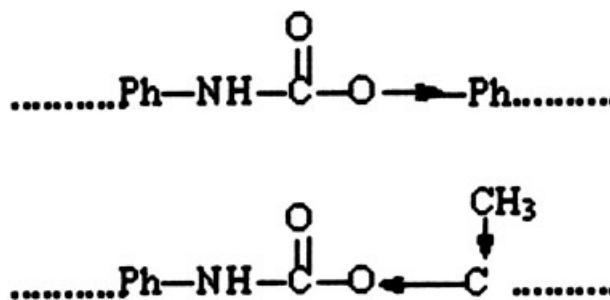


Figure 3 TGA curves of NR/PU block copolymer: (a) NR/EG (70/30), (b) NR/EG (50/50), (c) NR/EG (30/70), (d) NR/PG (70/30), (e) NR/1,3-BDO (50/50), (f) NR/1,4-BDO (30/70) and (g) NR/BPA(40/60).

that the present block copolymers are completely phase separated systems.

Thermal degradation kinetics

The kinetic parameters for the thermal degradation of the block copolymers synthesized were derived from the TGA curves by applying an analytical method proposed by Coats and Redfern.²⁰ In solid state thermal decomposition reactions, which are generally homogenous in nature, the mechanism is



Scheme 4 Electronic effect in urethane linkage.

TABLE IV
Kinetic Parameters from the Thermal Degradation of the NR/PU Block Copolymers

Sample	Activation energy E (kJ/mol)		Arrhenius parameter A (s ⁻¹)		Entropy of activation ΔS (J/deg/mol)	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
NR/EG(70/30)	99.88	227.65	16.1	57814.6	-227.65	-160.58
NR/EG(50/50)	81.64	143.61	1.0	42.6	-250.38	-220.67
NR/EG(30/70)	125.08	210.12	119.3	54819.3	-210.78	-161.13
NR/PG(70/30)	88.06	395.12	2.9	3.42×10^{10}	-241.79	-49.86
NR/PG(50/50)	110.70	335.33	15.2	3.17×10^8	-227.82	-88.96
NR/PG(30/70)	122.38	271.64	80.1	166.1	-214.05	-132.72
NR/1,3-BDO(70/30)	119.97	169.75	101.7	542.97	-211.85	-199.02
NR/1,3-BDO(50/50)	224.75	367.07	1985537	1.06×10^9	-129.86	-78.99
NR/1,3-BDO(30/70)	225.17	341.65	2197887	3.22×10^8	-129.04	-88.90
NR/1,4-BDO(70/30)	99.06	317.50	11.0	8.34×10^7	-230.24	-99.78
NR/1,4-BDO(50/50)	147.02	149.23	836.9	75.71	-194.43	-215.60
NR/1,4-BDO(30/70)	120.99	400.55	53.1	5.51	-217.30	-172.12
NR/BPA(70/30)	137.29	174.98	1746.2	430.57	-187.68	-201.08
NR/BPA(50/50)	252.80	252.73	60107.2	59759.5	-160.31	-160.30
NR/BPA(40/60)	125.62	208.36	337.5	61213.4	-201.00	-160.20

governed by three fundamental aspects, viz., the laws of diffusion, nucleus formation and its growth and phase-boundary movements.²¹ Overall rate of decomposition is controlled by these processes. The most prominent rate controlling process operating in a particular case is chosen and used for deriving the rate equations. The integral equation was used in the form,

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}$$

where $g(\alpha)$ is the kinetic model function, α is the decomposed fraction at any temperature, T , ϕ is the heating rate, A is a numerical constant, and E stands for activation energy. A plot of the above integral equation against $1/T$ gives a straight line with slope = E/R and intercept = $\ln (AR/\phi E)$. Entropy of activation ΔS was calculated using the relation,

$$A = \frac{kT_s}{h e^{\frac{\Delta S}{R}}}$$

where A is the pre-exponential factor, k the Boltzmann constant, h is the Planck's constant and T_s the peak temperature in the DTG curve.

All the TGA data were analyzed using the nine mechanistic equation proposed by Satava²² and their kinetic parameters were calculated. It was found that the Ginstling-Brounshstein equation $(1 - 2/3a) - (1 - a)^{2/3}$ best represents the experimental data and gives a mechanism of the reaction in all samples, which corresponds to a three dimensional diffusion mechanism for the solid state thermal decomposition.

The kinetic parameters for the two stage thermal decomposition of the NR/PU samples (Table IV)

show that the activation energy for the first stage degradation is lower than that of the second stage. Higher activation energy of the NR soft segments in the second stage indicates that they are more thermally stable than the polyurethane segments.

The negative values of the entropy of activation (ΔS) in both stages of the thermal decomposition of the copolymers suggest that the segments undergo some chain alignment at elevated temperatures forming the activated complex. This interim order is more pronounced in the hard segment decomposition and relatively less in the soft segment decomposition. The reason for this is the higher interaction through hydrogen bonding and dipolar interaction in the polyurethane part, leading to greater ordering in the activated complex compared to the soft segment. This is reflected in the magnitude of the entropy change which is more in the first stage than in the second stage. No gradation in values of ΔS and E with variation in composition is observed in both the stages. However, in the first stage of degradation E seems to be low for the 70/30 composition in which polyurethane content is the lowest, where much intermolecular attraction is not expected due to the formation of shorter chains. The soft segment is devoid of polar interaction and thus no gradation in the activation energy is observed.

CONCLUSIONS

Block copolymers based on NR and different PUs have been synthesized and characterized. All the samples of the block copolymers in five series, viz., NR/EG, NR/PG, NR/1,3-BDO, NR/1,4-BDO, and NR/BPA exhibit a two-stage degradation pattern showing the presence of two phases. First stage

degradation corresponds to the polyurethane and the second stage is caused by the NR phase. Onset temperature of the first stage degradation remains very close to each other with aliphatic chain extenders, viz., EG, PG, 1,3-BDO, and 1,4-BDO in the range 200 to 250°C, but samples with BPA exhibit much lower onset temperature due to their lower thermal stability compared to the aliphatic polyurethanes. Second stage degradation is unaffected by the type of polyurethane and NR content, which implies that phase interaction between NR and PU is absent. Thus the NR/PU block copolymers containing aliphatic chain extenders are more stable than NR/BPA block copolymers and these block copolymers are phase separated systems. The kinetic studies on the solid state thermal decomposition of the samples show that there are two activation energy values for each sample indicating again complete or almost complete phase separation. The DSC analysis of the block copolymers also shows that they are made up of two different phases since the thermograms exhibit transitions due to the NR phase (−60 to −65°C) and the polyurethane phase (76 to 110°C). Variation in the T_g of the polyurethane phase reflects the different level of chain flexibility caused by the different chain extender diols. Beyond the T_g of PU phase and at higher temperature all the samples show exotherms which are attributed to the crystallization of hard segments. This is followed by strong endotherms identified as the melting with degradation of these segments.

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