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Swelling characteristics of NR/PU block copolymers and the effect of NCO/OH ratio on swelling behaviour

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Abstract

A series of (NR/PU) block copolymers (BCs) was prepared from toluene diisocyanate (TDI), 1,3-butane diol (1,3-BDO), and hydroxyl-terminated liquid natural rubber (HTNR), by solution polymerisation. The swelling characteristics of the BCs were investigated. Diffusion profile in various solvents and the sorption kinetics were studied. Arrhenius and thermodynamic parameters were evaluated from the diffusion data. Finally, the influence of NCO/OH ratio on the swelling behaviour was also studied. The equilibrium sorption value (Q_∞) decreased with increasing NCO/OH ratio for all the BCs. The samples have higher uptake of solvents with solubility parameter within a small range centred about 9 $(\mathrm{cal/cm^3})^{1/2}$. Highly polar and non-polar solvents show minimum uptake. It was observed that polarity factor predominates in the solvent transport through the present block copolymer systems. The sorption behavior is also found to vary with the NCO/OH ratio employed in the preparation of polyurethane (PU) oligomers.

Keywords: Block copolymer; Natural rubber; Swelling behaviour

1. Introduction

The growing interest in the exploitation of renewable sources in the general areas of energy and materials has been one of the major scientific and technological issues of the past few decades and this trend seems likely to be pursued. Hence, much attention has been focused on the innovation and development of newer materials from renewable sources. Natural rubber (NR) is one of the cheaply and abundantly occurring materials. Our laboratory has been investigating the possibility of developing new polymeric materials from natural rubber. This has lead to the synthesis of natural rubber based block polymers. 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.

Polyurethane (PU) block polymers form an important class of thermoplastic elastomer whose properties are derived from the microphase separation in the solid state. Important variables affecting properties include segment length, segment polydispersity, degree of phase separation, crystallinity and processing history. Segmented polyurethane block copolymers are usually composed of a polyether or polyester soft segment and urethane hard segment. 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 [1,2]. This is reflected in the swelling characteristics of these blocks copolymers. The molecular transport of organic solvent in polyurethane polymers is a subject of both fundamental and technical importance. One of the earliest transport studies in polyurethane elastomers compared to the transport properties of commercial polyurethanes having different types of soft segments, viz. elastomer, polyesters and polyethers was reported. The effect of varying the hard segment length, the hard segment composition, and the type of soft segment on the transport properties in polyether and polyester polyurethanes was considered by McBride et al. [3]. Hydroxy-terminated polybutadiene-based prepolyurethanes and diamine chain extended polyurethane-ureas were prepared and treated with various organic solvents in the moisture-cured state in order to modify their ultimate strength [4]. Sorption and diffusion of a number of chlorinated alkanes

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through a diol chain extended polyurethane (PU) membrane have been investigated and reported [5]. In general, the transport of organic solvents through polyurethane is interesting due to its two-phase morphology, there by controlling the mechanism of transport in a peculiar manner.

In the present work, transport behaviour of organic solvent through block copolymer systems consisting of NR soft segments and PU hard segments has been investigated. The shape of diffusion profile, sorption kinetics, the transport coefficient including solubility (*S*), diffusion coefficient (*D*), and permeability (*P*) and sorption mechanism are described here. Effect of NCO/OH ratio on swelling behaviour of these block copolymer was also discussed.

2. Experimental

2.1. Materials

Natural rubber (NR), (ISNR-5): viscosity average molecular weight, $(\bar{M}_v) = 820,000$, intrinsic viscosity, $[\eta]$ 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. 1, 3-Butane diol (1,3-BDO) was supplied by Riedel-dettaën (Germany) and used as such. 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, Bombay (India). It was used without further purification. Hydrogen peroxide (30%) was obtained from Merck. India Ltd, Bombay, (India). Tetrahydrofuran (THF) (Reagent grade) supplied by Merck. India Ltd, Bombay, (India) was dried using sodium wire and distilled before use.

N,*N*-Dimethyl formamide (DMF) (Reagent grade) was obtained from Merck. India Ltd, Bombay, (India). It was distilled before use. Dimethyl sulphoxide (DMSO) (Reagent grade) was obtained from Merck India Ltd, Bombay, (India) which was used as such. Toluene, dichloromethane (DCM), carbon tetrachloride, cyclohexanone (all Reagent grade) supplied by Merck, India Ltd, Bombay, (India) were purified by distillation.

Hydroxyl terminated liquid natural rubber (HTNR) of number average molecular weight 4600 was prepared in the laboratory by the photochemical degradation of natural rubber as per reported procedure [6]. It was reprecipitated thrice from toluene using methanol and dried at 70–80 °C in vacuum.

Table 1
(NR/PU) block copolymer samples specifications

Sample	NCO/OH ratio	$\overline{DP}$ of PU segment	wt% Hard segment	wt% Soft segment
(NR/PU)-1	1.96	3	27.83	72.17
(NR/PU)-2	1.65	4	28.61	71.39
(NR/PU)-3	1.40	6	29.49	70.51
(NR/PU)-4	1.31	7	29.86	70.14
(NR/PU)-5	1.26	9	30.11	69.89

2.2. Synthesis of block copolymers

Dissolved 1,3-butane diol (0.0067 mol) in chloroform to get a 10% solution. Catalyst, DBTDL (about 0.5% by weight of TDI) was added to the solution in the reaction vessel. A known amount of TDI (0.011 mol) in chloroform was added to the above solution in small quantities during a period of 5 min. The reaction was allowed to continue for 1 h at 65 °C. Then, 8 g of HTNR $(\bar{M}_n = 4600)$ was made into a 20% solution in chloroform and added to the reaction mixture and the reaction was continued for 5 h. Finally the excess solvent was distilled off and the viscous polymer solution was poured into trays treated with silicon release agent and kept overnight for casting into sheets. The sheets were subjected to heat treatment at 60 °C for 24 h to remove residual solvent followed by 2 weeks aging at room temperature in a dry atmosphere. The polymer was characterized by infrared spectroscopy. The composition of the block copolymers and the hard segments length were varied by changing the molar ratio of the NCO to OH groups of TDI/1,3-BDO in the range 1.96–1.26.

2.3. Polymer designation

Samples of block copolymers are named as (NR/PU)-1 to (NR/PU)-5 as shown in Table 1. (NR/PU) stands for the block copolymer and the number indicate the serial order of synthesis with decreasing NCO/OH ratio from 1.96 to 1.26, respectively. Here also the number indicates the NCO/OH ratio by which it was prepared as shown in Table 1.

2.4. Measurements

2.4.1. Swelling experiment

Circular shaped samples (diameter ~13 mm) were cut from the block copolymer sheets and the thickness of the samples was measured with an accuracy of ±0.01 mm. Dry weight of the cut samples were taken before immersion into THF at room temperature (RT). The samples were periodically removed from test bottles and the adhering solvent blotted off the surface. Then the samples were weighed on an electronic balance (Shimadzu, Libor AEU-210, Japan) and immediately replaced into the test bottles. This procedure was continued until equilibrium swelling was attained in the case of each sample. The time taken for each weighing was kept constant to a minimum of 20–30 s in order to avoid errors due to the escape of solvent from the samples. The results of these experiments were expressed as moles of solvent uptake by 100 g of polymer sample, Q_t (mol%).

3. Results and discussion

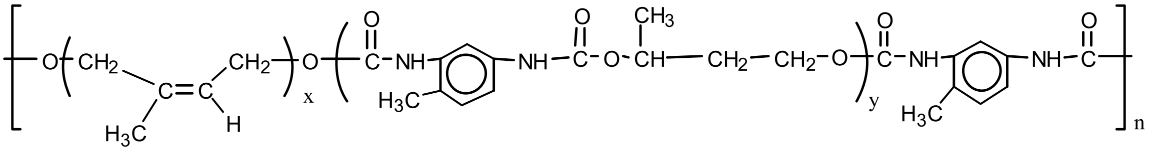
Samples under study were prepared by the block copolymerisation of liquid NR and polyurethane oligomers as per reported procedure [7–11]. The polyurethane oligomers were derived from 1,3-butane diol and toluene diisocyanate. Two-shot block copolymerisation method was adopted in which the NCO endcapped PU oligomers were formed first and chain extended with liquid NR. The samples have a block copolymer structure as shown in Scheme 1 [7]. The value of x is about 68 as calculated from the molecular weight of HTNR, viz., 4600. The degree of polymerisation of the PU segment is denoted by n. Its value varies with the NCO/OH ratio used in the respective synthesis. Determination of this entails a knowledge of the molecular weight of the PU segments. However, since the solubility of the PUs is limited, molecular weight determination was not possible. Hence the n values were obtained by theoretical considerations. Degree of polymerisation ($\overline{\mathrm{DP}}$) of a PU segment is calculated using the relation $\overline{\mathrm{DP}} = (1+r)/(1-r)$ where r is the stoichiometric imbalance in the concentration of NCO and OH groups given by the ratio of the lesser quantity functional group to excess functional group. The calculated values of $\overline{\mathrm{DP}}$ are given in Table 1. Thus, PU segments in (NR/PU)-5 possess a $\overline{\mathrm{DP}}$ of about 9 which corresponds to an NCO/OH ratio of 1.26. The $\overline{\mathrm{DP}}$ value decreases to 7, 6, 4 and 3 for PUs in (NR/PU)-4, (NR/PU)-3, (NR/PU)-2 and (NR/PU)-1 corresponding to the NCO/OH ratio of 1.31, 1.4, 1.65 and 1.96. Thus, these block copolymers are differentiated on the basis of the NCO/OH ratio as shown in the Table 1. The variation in the NCO/OH ratio does not, however, change substantially the weight per cent composition of the soft and hard segments in the block copolymers. It is kept around 70 wt% of NR and 30 wt% of PU with small variation brought about individually by varying the NCO/OH ratio as shown in the Table 1. It is seen that the weight per cent composition changes in a small range only, viz. 69.89–72.17% in the case of NR and 30.11–27.83% in the case of PU.

Since, the weight percentage of PU is kept almost constant in all samples the variation in its $\overline{\mathrm{DP}}$ results in the formation of varying number of PU molecules during synthesis. Thus, PU in (NR/PU)-5 with the NCO/OH ratio of 1.26 yields lesser number of molecules than that of PU in (NR/PU)-1 with the NCO/OH ratio of 1.96. As the weight percentage of NR is also almost constant in all the synthesis, where ever there is excess PU molecules they, being NCO end capped, tend to crosslink the block copolymers through allophanate linkages (Scheme 2). Consequently the resulting products would be network polymers as seen in the present synthesis.

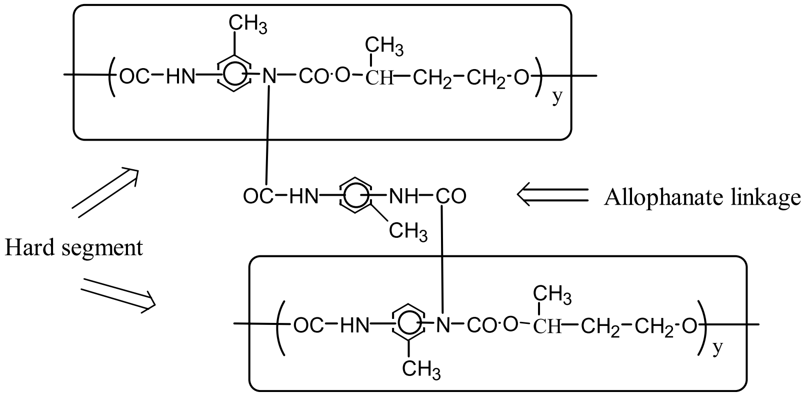
All the samples were subjected to sorption studies in different solvents (Table 2). The solvents were selected in terms of their polarity beginning with the non-polar toluene to the highly polar solvents, viz. DMF and DMSO. This is significant in the present systems since they possess multiphase with non-polar NR segments and polar PU segments.

3.1. Diffusion profile

Data from sorption studies are presented as plots of the percentage uptake of the penetrant against $t^{0.5}/h$, where t is the time and h is the thickness of the sample. These plots are referred to as reduced sorption plots since the sample thickness is included in the abscissa. Sorption plot for a representative sample, viz. (NR/PU)-1 in a total number of eight solvents is presented in Fig. 1. The percentage of solvent uptake gradually increases with time and then reaches an equilibrium value. This is the trend shown in all the solvents. However, there is variation in the equilibrium sorption value as well as the time taken to attain the equilibrium in different solvents. The attainment of sorption equilibrium was found to be much quicker in the case of chloroform, DCM and THF compared to other solvents. Longer time was taken by cyclohexanone and the non-polar toluene and highly polar DMF and DMSO. This observation is valid for all the samples studied. A similar trend is also seen in the case of the equilibrium uptake of the solvents by all the samples as shown in Table 2. The solvent uptake is found to be high for THF, chloroform and DCM but it is low for toluene, DMF and DMSO. Equilibrium extent of swelling and the rate of solvent uptake for a typical sample, viz. (NR/PU)-5 have been analysed with various parameters related to the solvents such as molar volume, solubility parameter, density and molecular weight. However, it was found that correlation exists only with the



Scheme 1. (NR/PU) Block copolymer structure.



Scheme 2. Allophanate croslinking in (NR/PU) block copolymers.

solubility parameter of the solvents for the present polymer–solvent systems. This is shown in Fig. 2.

The samples have higher uptake of solvents with solubility parameter [12] within a small range centred about 9 $(\text{cal/cm}^3)^{1/2}$. Solvent with solubility parameter of 9.52 $(\text{cal/cm}^3)^{1/2}$, viz. THF, was found to show the maximum amount of uptake. Solvents with both lower and higher solubility parameter values give only low equilibrium uptake (Table 2). The values show that polymers in THF have about 3–4 times higher uptake than in the non-polar toluene, carbon tetrachloride, and polar DMF and DMSO. This observation throws light on the block copolymer structure of the samples and the nature of the two types of blocks present in them. Highly polar and non-polar solvents interact only with the appropriate phase in the sample and the other phase excludes them so that the equilibrium uptake of the solvent has a lower value. Intermediate solvents such as THF interact with both the phases leading to higher uptake (Table 2). All these observations suggest that polarity factor predominates in the solvent transport through the present block copolymer systems.

3.2. Mechanism of sorption

The dynamic sorption data of the polymer–solvent systems for a circular geometry of the sample before 55% equilibrium sorption have been fitted to the following empirical formula [13,14].

$$\frac{Q_t}{Q_\infty} = kt^n \tag{1}$$

where Q_t and Q_∞ are the mole per cent increase in sorption at time t and at equilibrium, respectively. In order to investigate the type of diffusion mechanism, the sorption data of the penetrant–polymer systems have been analysed in terms of the empirical relation.

$$\log\frac{Q_t}{Q_\infty} = \log k + n\log t \tag{2}$$

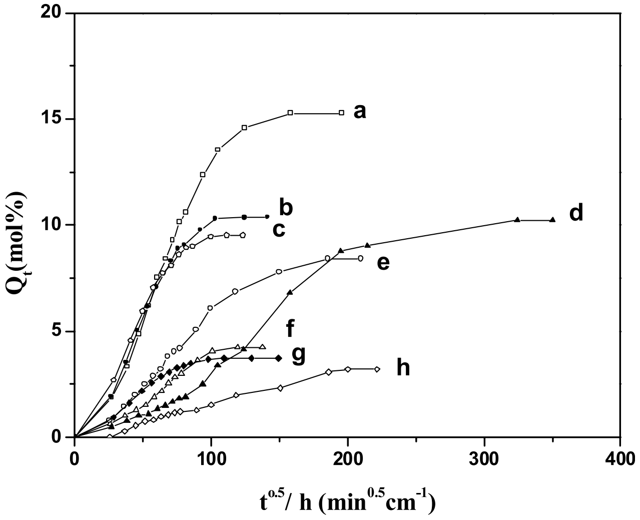


Fig. 1. Percentage mass uptake for (NR/PU)-1 in different solvents at RT; (a) THF, (b) chloroform, (c) DCM, (d) cyclohexanone, (e) carbon tetrachloride, (f) toluene, (g) DMF, (h) DMSO.

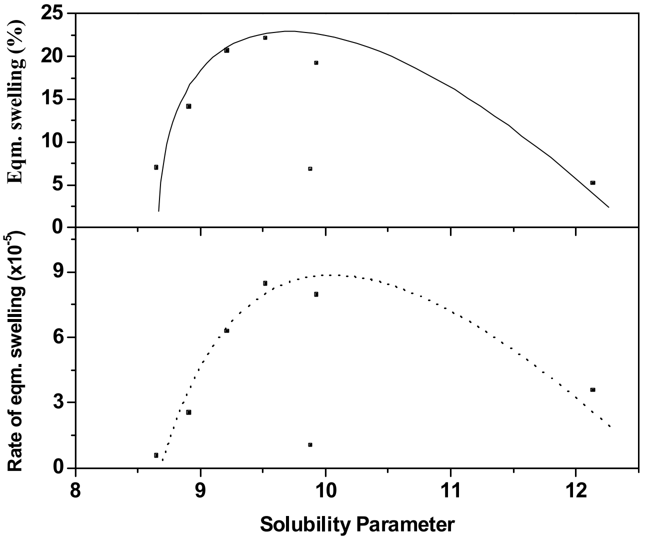


Fig. 2. Equilibrium swelling and rate of equilibrium sorption of (NR/PU)-5 sample versus solubility parameter of the solvents.

Table 2
Equilibrium uptake of solvents by the (NR/PU) block copolymers (Q_∞ mol%)

Penetrant	Penetrant solubility parameter [a] $(\mathrm{cal/cm^3})^{1/2}$	(NR/PU)-1	(NR/PU)-2	(NR/PU)-3	(NR/PU)-4	(NR/PU)-5
THF	9.52	11.60	15.26	17.91	19.152	22.16
Chloroform	9.21	8.58	10.49	13.87	14	20.67
DCM	9.93	8.43	9.51	12.34	12.43	19.20
Cyclohexanone	9.88	8.12	8.82	10.23	12.34	14.16
Carbon tetrachloride	8.65	5.61	8.40	5.09	6.68	6.97
DMF	12.14	3.19	3.57	4.23	5.04	5.19
Toluene	8.91	2.81	3.73	3.79	4.63	6.84
DMSO	12.93	1.82	2.59	3.20	3.79	3.93

[a] Data taken from Ref. [12].

The parameter k and n have been determined from a least square fit of the experimental log Q_t/Q_∞ versus log t (Fig. 3). The values are tabulated in Table 3. Constant k depends on the structural features of the polymer system and its interaction with the solvent used. The value of n provides information about the mechanism of solvent transport. When the value of n is 0.5, the sorption mechanism is Fickian and the rate of polymer chain relaxation is higher than the diffusion rate of the penetrant. When $n=1$, the diffusion mechanism is said to be non-Fickian where the chain relaxation is slower than the solvent diffusion. If the values lie between 1 and 0.5, then the mechanism is said to follow anomalous trend where the polymer chain relaxation rates and the solvent diffusion rate are similar.

The values of n in the present studies vary between 0.54 and 0.95 in the investigated temperature range. For solvents like toluene, DMF, DMSO and cyclohexanone the values of n are found to be in between 0.50 and 0.70 which suggest that the transport mechanism is very close to Fickian mode with the rate of chain relaxation tend to be greater than the diffusion rate of the penetrant. There are solvents with extreme characteristics in this group, i.e. highly polar and non-polar solvents. They tend to plasticize the respective blocks leading to greater relaxation. Moreover, the major constituent of the copolymer, viz. NR segments, is above its T_g contributing to the segment relaxation. All these suggest that the transport of these solvents occurs by a diffusion controlled mechanism.

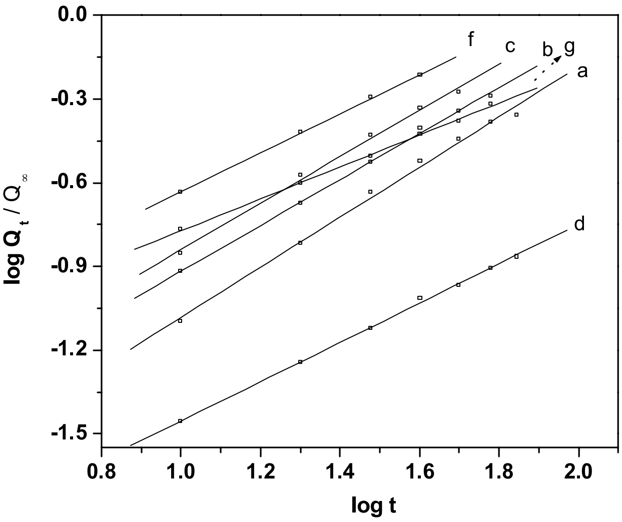


Fig. 3. Plot of log Q_t/Q_∞ versus log t for (NR/PU)-5 block copolymer in various solvents; (a) THF, (b) chloroform, (c) DCM, (d) cyclohexanone, (f) toluene, (g) DMF.

For THF, chloroform, DCM and carbon tetrachloride the values of n are higher but less than one suggesting anomalous sorption behaviour where the rate of relaxation and diffusion are comparable. This anomalous behaviour for the solvents may be due to the interaction of the polar and non-polar segments of the polymer matrix almost equally with the solvents. Thus, time will be taken by the PU hard segment to respond to the swelling stress and rearrange themselves to accommodate the solvent molecules.

The values of k do not show a regular trend. In the case of chemically similar solvents, as the molecular mass of the solvent increases there is a decrease in the value of k. Combined effect of the polarity of the solvent and size of the penetrant as well as the presence of both polar and non-polar segments in the block copolymer determine the value of k.

3.3. Sorption kinetics

Sorption and diffusion of liquid through polymer membranes are accompanied by structural rearrangement in the polymer matrix and this induces kinetic behaviour. The kinetic rate constant is a measure of the speed with which a solvent molecule penetrates the medium. An attempt has been made here to analyse the sorption data in terms of the first order kinetic model. Thus the first order rate constant k_1 for the polymer–solvent systems was estimated using the following first order rate equation.

$$\frac{\mathrm{d}c}{\mathrm{d}t} = k_1(C_\infty - C_t) \tag{3}$$

C_∞ and C_t are the concentration of penetrant at equilibrium and time t, respectively. Q_∞ is the equilibrium swelling and Q_t is swelling at time t. Integration of Eq. (3) gives,

$$k_1 t = 2.303 \log\left(\frac{C_\infty}{C_\infty - C_t}\right) \tag{4}$$

Table 3
Swelling characteristics in terms of k and n values of (NR/PU) block copolymers at 27 °C

Penetrant	(NR/PU)-1		(NR/PU)-2		(NR/PU)-3		(NR/PU)-4		(NR/PU)-5	
	n	k	n	k	n	k	n	k	n	k
THF	0.87	1.85	0.86	1.64	0.88	1.77	0.89	1.04	0.9	1.64
Chloroform	0.93	2.08	0.82	2.82	0.82	2.4	0.82	1.18	0.88	1.24
DCM	0.69	6.24	0.72	5.35	0.7	4.9	0.83	2.12	0.94	1.44
Cyclohexanone	0.67	3.24	0.66	2.39	0.6	2.05	0.57	2.8	0.59	2.12
Carbon tetrachloride	0.82	1.18	0.78	1.59	0.74	2.53	0.69	3.6	0.69	3.02
DMF	0.66	2.81	0.66	3.24	0.66	3.47	0.69	4.62	0.66	3.02
Toluene	0.62	6.34	0.62	4.4	0.63	2.36	0.7	4.68	0.61	4.37
DMSO	0.54	1.29	0.63	1.14	0.61	1.45	0.56	0.69	0.65	0.86

Unit; $k\times10^{2}$ g g^{-1} min^{n}.

The values of rate constant obtained by the least square analysis of log $C_\infty-C_t$ against time t are given in Table 4 and the typical plots are given in Fig. 4. For all penetrants these plots exhibit a decreasing trend with a negative slope from THF to cyclohexanone. The penetrants such as THF, chloroform and DCM show high rate constant values. They were in the range (7–19)$\times10^{3}$ min^{-1}. Other penetrants give only low values for the rate constant, (0.56–9.67)$\times10^{3}$ min^{-1} among the samples studied. The value is highest for THF and least for cyclohexanone. Kinetic rate constant values were found to decrease with non-polar solvents and also solvents with high polarity. This finding agrees well with the earlier observations regarding equilibrium swelling and the rate of solvent absorption.

For extensive swelling, the thickness of the sample obviously does not remain constant and hence, the diffusion coefficient increases due to the sorption of the penetrant into the polymer matrix. If swelling becomes considerable, then it is legitimate to apply second-order kinetics. Schott explained the use of second order kinetics for swelling experiments [15]. The equation used to evaluate the second order swelling is

$$\frac{\mathrm{d}c}{\mathrm{d}t}=k_2(C_\infty-C_t)^2 \tag{5}$$

where k_2 is the second order rate constant. The integrated form of the equation representing the swelling rate at time t is given by:

$$C_t=\frac{k_2C_\infty^2t}{1+k_2C_\infty t} \tag{6}$$

which on further simplification gives

$$k_2t=\frac{C_t}{C_\infty(C_\infty-C_t)}\text{ or }k_2t=\frac{1}{C_\infty-C_t}-\frac{1}{C_\infty} \tag{7}$$

Second order kinetic plots for a representative sample, viz.; (NR/PU)-5 block copolymer in different solvents are given in Fig. 5. The slope of the plots gives the values of k_2 which are compiled in Table 4. The k_2 values were obtained in the range (5.99–14.5)$\times10^{-2}$ min^{-1} mol^{-1} for THF, chloroform and DCM and did not follow any systematic trend. Because a straight line was obtained for first order kinetics for all solvents used, it seems to be the kinetics for the transport of organic penetrant in (NR/PU) block copolymers.

3.4. Diffusion coefficient

Diffusion through a polymer occurs when small molecules pass through voids and other gaps between the polymer molecules. Diffusion rate will, therefore, depend on the size of the small molecules and the size of the gap in the polymer. The latter depends a large extent on the physical state of the polymer, i.e. whether glassy, rubbery or crystalline. For Fickian transport the rate of approach to equilibrium swelling can be characterised by a diffusion

Table 4
Kinetic data on the solvent uptake by the (NR/PU) block copolymers (k_1 is the first order rate constant and k_2 is the second order rate constant)

Penetrant	$k_1\times10^{3}$ (min^{-1})					$k_2\times10^{2}$ (min^{-1} mol^{-1})
	(NR/PU)-1	(NR/PU)-2	(NR/PU)-3	(NR/PU)-4	(NR/PU)-5	(NR/PU)-5
THF	8.3	9.3	14.4	17.6	19	5.49
Chloroform	7.8	9.6	12.7	13.4	14.16	10.6
DCM	7	7.86	9.63	11.2	12.69	14.5
Cyclohexanone	0.56	0.63	1.31	1.54	2.1	–
Carbon tetrachloride	3.62	5.35	6.9	8.74	9.67	–
DMF	1.02	1.45	2.3	3.5	4.8	94
Toluene	4.87	6.39	7.62	9.1	11	89.34
DMSO	0.68	0.89	1.2	2.65	3.5	–

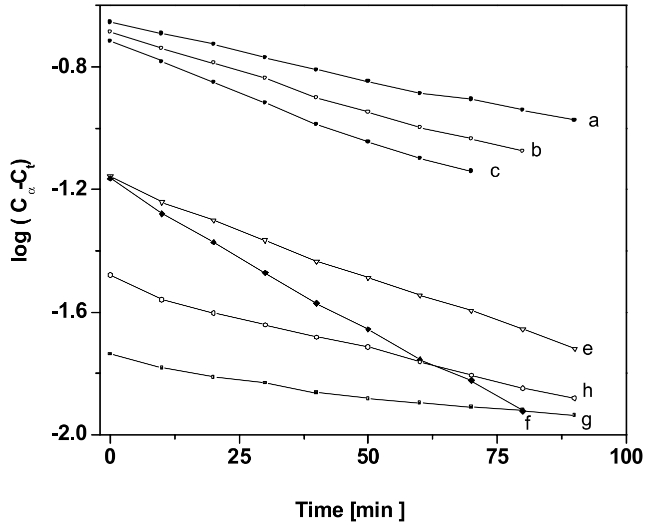


Fig. 4. log $C_\infty - C_t$ versus time for the solvent uptake by (NR/PU)-5 block copolymer; (a) THF, (b) chloroform, (c) DCM, (e) carbon tetrachloride, (f) toluene, (g) DMF, (h) DMSO.

coefficient. Fick's law is the most suitable equation for defining the diffusion coefficient.

The effective diffusivity or diffusion coefficient (D) of the polymer–solvent system is a kinetic parameter which can be calculated from the initial linear portion of the sorption curves using the following equation [16].

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \left\{ \left[\frac{1}{(2n+1)^2}\right] \exp\left[\frac{-D(2n+1)^2\pi^2 t}{h^2}\right] \right\} \tag{8}$$

where Q_t and Q_∞ are the mass of solvent uptake at time t and at equilibrium, respectively, h is the initial sample thickness. Although this equation can be solved readily, it is instructive to examine the short time limiting expression as well [17].

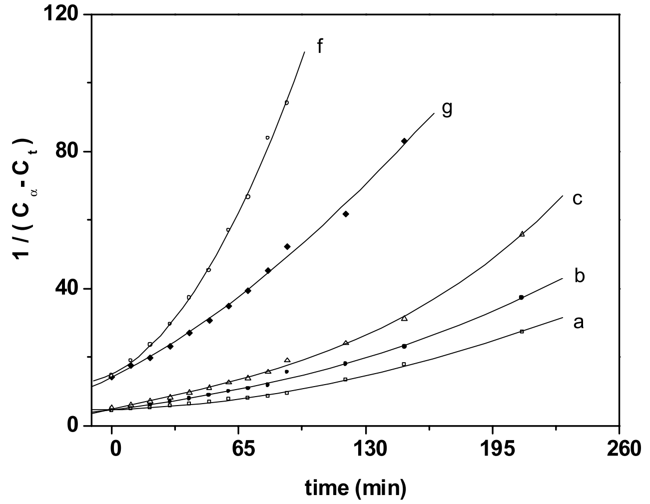


Fig. 5. Second order kinetic plots for the solvent uptake by (NR/PU)-5 blocks copolymer; (a) THF, (b) chloroform, (c) DCM, (f) toluene, (g) DMF.

$$\frac{Q_t}{Q_\infty} = \left[\frac{4}{\pi^{1/2}}\right] \left[\frac{Dt}{h^2}\right]^{1/2} \tag{9}$$

From a plot of Q_t versus $t^{0.5}/h$, a single master curve is obtained which is initially linear. Thus, D can be calculated [15] from a rearrangement of Eq. (9) as

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \tag{10}$$

where θ is the slope of the nearly linear portion of the sorption curve, i.e. before the attainment of 50% of equilibrium uptake (Fig. 1) and Q_∞ is the mole per cent increase in sorption at equilibrium. From this equation, it is understood that D is directly proportional to the slope and inversely proportional to the maximum solvent uptake. Because of considerable swelling in a short period, a swelling correction is necessary to get correct diffusion coefficient, known as the intrinsic diffusion coefficient (D^*). This can be calculated using the following equation [18],

$$D^* = \frac{D}{\phi^{7/3}} \tag{11}$$

where ϕ is the volume fraction of the polymer. The estimated values of the intrinsic diffusion coefficient of (NR/PU) samples are given in Table 5. The variation in D^* value depends on the nature of the crosslink, penetrant size and polarity.

Normally, the diffusion coefficient values decrease with increasing molecular size of the penetrant. It seems that this trend is not followed in the present case. Among the penetrants studied, THF and DMF are having low molecular weight values, viz. 72.11 and 73.1, respectively. However, the corresponding D^* values differ greatly. THF gives a value equal to 426 and DMF shows only a value of 7.82 for the sample, (NR/PU)-5. Similarly, all the penetrants show wide variations in the D^* values irrespective of the molecular weight as shown in the Table 6. The highest value is shown by THF and the lowest value is observed in the case of DMSO. Among the chlorinated penetrants, the highest value of 233 is shown by chloroform (molecular weight = 119.5) followed by carbon tetrachloride (molecular weight = 84.93) with a value of 41. Here, again no correlation is observed with the molecular size of the penetrants. To sum up, the D^* depends more on the molecular interaction between penetrants and the polymer than the penetrant molecular size. The very high values of D^* for THF are construed as the combined effect of the molecular interaction and its small molecular size. It is found that the decrease in D^* value on going from THF to DMSO is relatively small in the case of (NR/PU)-1 and high for (NR/PU)-5. Values of D^* for all other systems are in between them.

3.5. Sorption coefficient

In order to get a better understanding on the strength of interaction between polymer and solvents, the sorption

Table 5
Diffusion, sorption and permeation coefficients of various solvents in the block copolymers

Penetrant	(NR/PU)-1	(NR/PU)-2	(NR/PU)-3	(NR/PU)-4	(NR/PU)-5
Diffusion coefficient, $D^* \times 10^4$ ($cm^2\ s^{-1}$)					
THF	125	134	203	249	426
Chloroform	57	71	95	111	233
DCM	32	37	40	78	146
Cyclohexanone	4	5	6.6	8.68	17.6
Carbon tetrachloride	8	13	18	26	41
DMF	2.46	3.7	4.54	6.19	7.82
Toluene	8.94	2.67	4.68	7.45	29.4
DMSO	0.53	0.60	0.86	1.55	1.69
Sorption coefficient, S ($g\ g^{-1}$)					
THF	8.86	11	12.91	13.8	15.98
Chloroform	10.64	12.53	16.58	16.73	24.71
DCM	6.64	8.08	10.02	10.55	16.31
Cyclohexanone	8.03	8.65	10.04	12.57	13.89
Carbon tetrachloride	5.6	7.83	8.97	10.73	12.93
DMF	2.69	3.09	3.68	3.79	3.42
Toluene	2.49	3.43	3.49	4.27	6.31
DMSO	1.42	2.18	2.5	3.17	3.07
Permeation coefficient, $P \times 10^4$ ($cm^2\ s^{-1}$)					
THF	1107	1474	2620	3436	6807
Chloroform	606	889	1575	1857	5757
DCM	212	298	400	822	2381
Cyclohexanone	32	43	66	109	244
Carbon tetrachloride	44	101	161	278	530
DMF	6.6	11	16	23	26
Toluene	22	9	16	31	185
DMSO	0.75	1.3	2.15	4.7	5.3

coefficient, (S), which is a thermodynamic parameter has been calculated using the relation,

$$S = \frac{M_S}{M_P} \tag{12}$$

where M_S is the mass of the penetrant molecules at equilibrium swelling and M_P is the initial mass of the polymer sample [19]. It is found that S is maximum for chloroform–polymer system and minimum for DMSO–polymer system (Table 5). The higher value for THF is an indication of the better accommodation of the solvent molecules due to favourable interaction with the hard domains as well as the soft NR matrix and also due to the small size of the penetrant. The minimum value for toluene is explained by the fact that it being non-polar, is unable to interact with the polar PU segments, which are involved in the formation of domains resulting in physical crosslinking. Since the physical crosslinks are intact the NR segments held by them could absorb solvent only to limited levels.

Table 6
E_D, E_P and ΔH_S values for solvent uptake in the (NR/PU)-5 block copolymer

Penetrant	E_D ($kJ\ mol^{-1}$)	E_P ($kJ\ mol^{-1}$)	ΔH_S
THF	1.08	1.38	0.3
Chloroform	1.2	1.3	0.1
Cyclohexanone	1.47	4.4	2.93
Carbon tetrachloride	1.91	2.45	0.54
DMF	3.14	6.1	2.96
Toluene	1.76	4.5	2.74
DMSO	3.3	12.0	8.7

3.6. Permeation coefficient

The process of permeation is a combined effect of diffusion and sorption and thus the permeability coefficient, (P) depends on both D and S. Therefore, P can be calculated using Eq. (13).

$$P = DS \tag{13}$$

This relationship holds for the permeation process when the material obeys Fick's law and Henry's law. P values in different solvents are given in Table 5. It is found that the value is highest for THF and chloroform and minimum for DMSO. The D^* is the average capacity of the penetrant molecules to move among the polymer chain segments and S is a thermodynamic function which depends on the equilibrium sorption value. P reflects the net effect of sorption and diffusion. Compared to D^* and P, the value of S is higher and this indicates a large tendency of penetrant to dissolve or sorb into the polymer. From this, it is possible to conclude that sorption predominates over diffusion in the permeation process of the system under study.

3.7. Arrhenius parameters

From the temperature dependence of the transport coefficients (D, P and S), one can estimate the activation parameters (E_D, E_P and ΔH_S) for the processes of diffusion, permeation and sorption. The following relation [20] has been used for the diffusion process.

$$\log D^* = \log D_0 - \frac{E_D}{(2.303RT)} \tag{14}$$

where E_D represents the activation energy of diffusion, which is a function of the intra and inter chain forces. These must be overcome in order to create the space for a unit diffusional jump of the penetrant molecule. D_0 is a constant and R is the gas constant and T is the temperature in absolute scale. The activation energy will be greater as the penetrant molecule is larger, the polymer cohesive energy is higher, and the polymer chain segments are more rigid. Similarly, P can be expressed [21] in terms of the van't Hoff's equation.

$$\log P = \log P_0 - \frac{E_P}{(2.303RT)} \tag{15}$$

Here E_P is the activation energy for permeation. Since P is a combination of diffusion and sorption process the activation energy, E_P for permeation is given as

$$E_P = E_D + \Delta H_S \tag{16}$$

Eqs. (14) and (15) were used to determine E_D and E_P based on Fig. 6 which displays the dependence of log D^* and log P on $1/T$. E_D values vary from 1.08 to 3.3 kJ mol^{-1} from THF to DMF (Table 6). The value is highest for DMF and lowest for THF. Same trend is observed for E_P values also. Highest values which lie in the range 6–12 kJ mol^{-1} are shown in DMF, DMSO and cyclohexanone and lowest value of 1.3 kJ mol^{-1} in chloroform. Highest value for DMF and DMSO may be due to the unfavourable interaction with the NR phase and the highest value shown by toluene is explained on the basis of unfavourable interaction with the PU phase. THF and chloroform are showing lower values of E_D. This is consistent with their higher values of different coefficients. From Eq. (16) ΔH_S values were calculated (Table 6) and it is found that the values for all the solvents were positive, which suggests that the sorption was an endothermic process and the sorption proceeded through the creation of new sites or pores in the polymer. All these observations show that diffusion of the penetrants is controlled by thermodynamic factors rather than the penetrant size or their molecular mass which do not exhibit any correlation with the activation energy values.

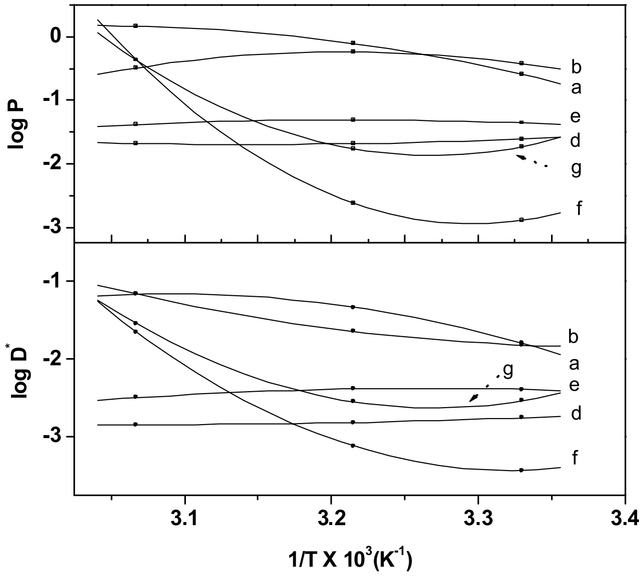


Fig. 6. log D^* and log P versus $1/T$ for the (NR/PU)-5 block copolymer; (a) THF, (b) chloroform, (d) cyclohexanone, (e) carbon tetrachloride, (f) toluene, (g) DMF.

Table 7
Thermodynamic parameters for the solvent uptake by the (NR/PU)-5 block copolymer

Penetrant	ΔH^0 (kJ mol^{-1})	$-\Delta S^0$ (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	K_S
THF	0.65	0.86	0.91	0.221
Chloroform	0.59	1.2	0.94	0.206
Cyclohexanone	1.4	1.2	1.76	0.141
Carbon tetrachloride	0.62	1	1.6	0.084
DMF	0.98	2	1.6	0.051
Toluene	0.6	3	1.61	0.068
DMSO	1.7	1.7	2.2	0.039

3.8. Thermodynamic parameters

Thermodynamic sorption constant, (K_S) gives a further understanding of the uptake of solvent by polymer [22]. The effect of penetrant characteristics on the K_S value can be seen in Table 7. THF showed a high K_S value. The trend is exactly same as that for Q_∞ values. K_S values decrease from THF to DMSO. Enthalpy (ΔH^0) and entropy (ΔS^0) values were calculated by plotting log K_S versus $1/T$ as per Eq. (17) for the different samples in various penetrants (Fig. 7). The corresponding free energy (ΔG^0) values could be obtained from these data.

$$\log K_S = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{17}$$

From the slope and intercept of the plot, $\Delta S^0$and ΔH^0 values were obtained. The ΔG^0 of the process was calculated from these values. It may be noted that for all the penetrants, the values of ΔH^0 are positive and they vary from 0.59 to 1.7 kJ mol^{-1} suggesting that the sorption of different solvents is also giving an endothermic contribution to the process. Hence, it was dominated by Henry's law mode, that is, the sorption proceeded through the creation of new sites or pores in the polymer. As shown in Table 7, ΔS^0

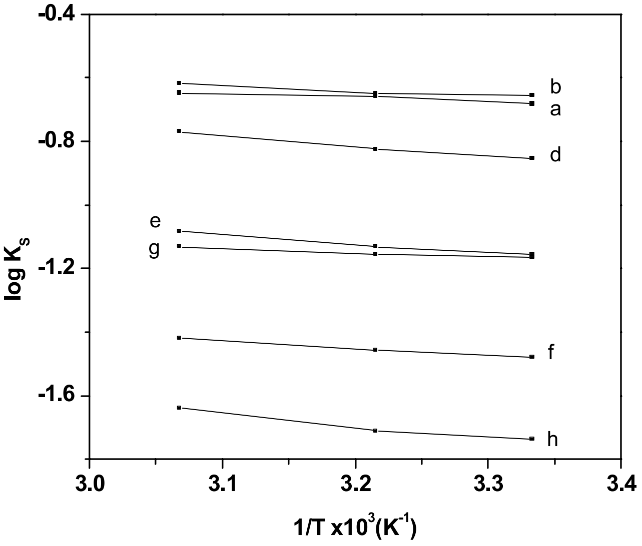


Fig. 7. Plot of log K_S versus $1/T$ for the (NR/PU)-5 block copolymer; (a) THF, (b) chloroform, (d) cyclohexanone, (e) carbon tetrachloride, (f) toluene, (g) DMF, (h) DMSO.

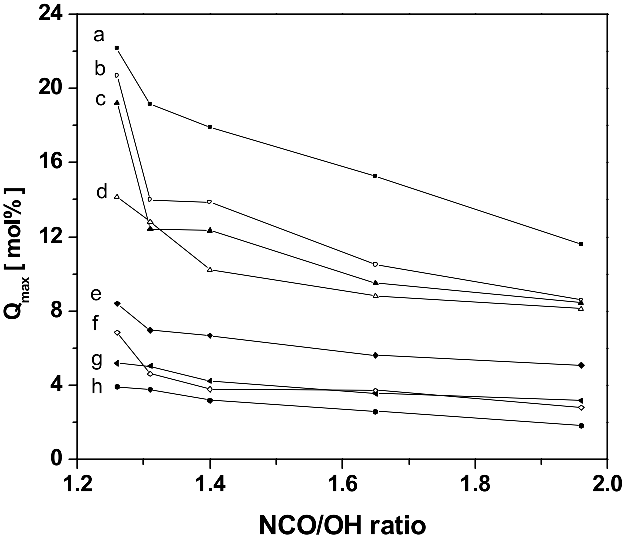


Fig. 8. Effect of NCO/OH ratio on the equilibrium swelling; (a) THF, (b) chloroform, (c) DCM, (d) cyclohexanone, (e) carbon tetrachloride, (f) toluene, (g) DMF, (h) DMSO.

values are negative for all the block copolymers, which suggest that the structure of the solvent molecules was retained even in the sorbed state. ΔS^0 values are in the range 0.86–3 J mol^{-1} K^{-1}. However, the ΔG^0 values are positive and small. The value for (NR/PU)-5 sample is lowest in THF and it is extreme in the case of toluene, DMF and DMSO. Thus the process is more spontaneous in THF and chloroform and less so in toluene, DMF and DMSO. It can be concluded that the sorption process is controlled predominantly by thermodynamic factors.

3.9. The effect of NCO/OH ratio on transport behaviour

Table 2 shows the variation in equilibrium sorption with NCO/OH ratio of the samples in all the solvents studied. The sorption values double in THF, chloroform and DCM as the NCO/OH ratio decreases from 1.96 to 1.26 in (NR/PU)-1 to (NR/PU)-5, respectively. About 75% increase is observed in cyclohexanone. Other solvents including two non-polar solvents, viz. carbon tetrachloride, toluene and two highly polar solvents, viz. DMF and DMSO show only small increase in the equilibrium sorption. In all cases, equilibrium sorption increases with decrease in the NCO/OH ratio irrespective of the nature of the solvents.

As the NCO/OH ratio is high the excess of NCO favours more crosslinking in the polymer systems. Higher level of crosslinking causes lower solvent uptake. Mechanism of sorption is not found to be influenced by the NCO/OH value. The Fickian and anomalous behaviour in different solvents described previously are valid at all NCO/OH ratios (Table 3) which indicates that the diffusion and relaxation phenomena are more solvent dependent than NCO/OH ratio. An increase in the *n* value with low NCO/OH ratio is observed only for THF and DCM solvents. However, the increase is observed within the limit of the anomalous region only.

Fig. 8 shows the variation of *P* with the NCO/OH ratio. It is found that the value increases almost ten fold with the decrease in NCO/OH from 1.96 to 1.26 in all solvents except DMF. This is the trend noted in the variation of D^* and *S* also with respect to the NCO/OH ratio as noted from Table 5. As this ratio decreases the level of crosslinking in the sample is also lowered which provides free volume facilitating the diffusion process. Thus, solvent penetration through the sample is enhanced at lower NCO/OH ratio. Although the general trend is an increase in the above properties with a decrease in NCO/OH ratio, significant increase is observed at the lowest value of NCO/OH, viz. 1.26. This is very pronounced in THF, chloroform and DCM as evidenced from the respective plot. Hence this value of NCO/OH ratio seems to be the optimum and it signifies the minimum required crosslinking in the samples to show higher level of solvent permeation (Fig. 9).

The variation in the thermodynamic parameters such as enthalpy and free energy for THF–polymer system is shown in Table 8. These parameters tend to decrease with a decrease in the NCO/OH ratio. A similar decrease is observed in the energy of activation for diffusion and permeation (Table 9). Decrease in all these parameters suggests that the polymer–solvent interaction is facilitated at lower values of the NCO/OH ratio.

4. Conclusion

Solvent with the solubility parameter of 9.52 (cal/cm^3)$^{1/2}$, viz. THF was found to show the maximum

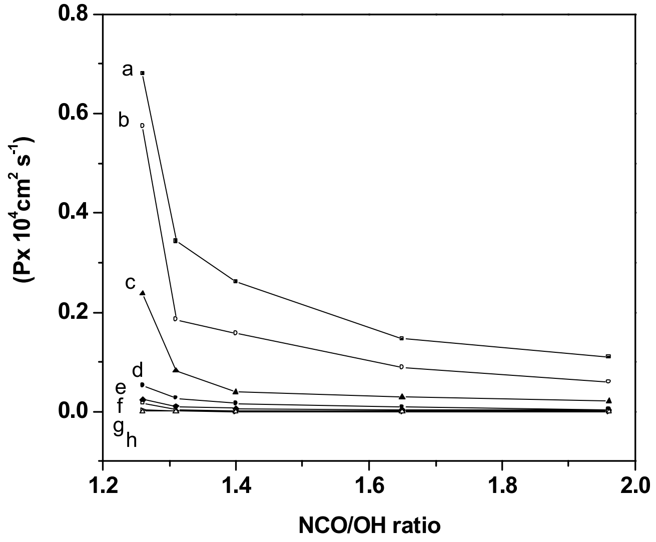


Fig. 9. Effect of NCO/OH ratio on the permeation coefficient; (a) THF, (b) chloroform, (c) DCM, (d) cyclohexanone, (e) carbon tetrachloride, (f) toluene, (g) DMF, (h) DMSO.

amount of uptake by all the samples. Those with lower and higher solubility parameter values than THF show only low equilibrium uptake. Transport of these highly polar and non-polar solvents show Fickian sorption mechanism, which is diffusion controlled mechanism since they tend to plasticize only the respective block leading to higher relaxation. But for THF, chloroform, DCM and carbon tetrachloride the transport is found to follow anomalous behaviour where the rate of relaxation and diffusion are comparable. This may be due to the interaction of the polar and non-polar segments of the polymer matrix almost equally with the solvents. The transport follows first order kinetics with highest rate constant for THF and lowest for cyclohexanone. Kinetic rate constant decreases with non-polar and highly polar solvents. All the penetrants show wide variations in the D^*, S and P values irrespective of the molecular weight. The highest value is shown by THF and the lowest value is observed for DMSO. Among the chlorinated penetrants, the highest value is shown by chloroform followed by carbon tetrachloride. The high value for THF is an indication of the better accommodation of the solvent molecules due to favourable interaction with the hard domains as well as the soft NR matrix and also due to the small size of the penetrant. The E_D is highest for DMF and lowest for THF. Same trend is observed for E_P values also. The ΔH^0 and entropy (ΔS^0) of the sorption process show highest values in DMF, DMSO and cyclohexanone and lowest value in chloroform. Highest value of DMF and DMSO may be due to the unfavourable interaction with the NR phase. Free energy of the process is positive suggesting that the sorption of different solvents is giving an endothermic contribution to the process. The value is lowest in THF and it is extreme in the case of toluene, DMF and DMSO. The sorption process is more spontaneous in chloroform and THF and less so in toluene, DMF and DMSO. It can be concluded that the process is controlled predominantly by thermodynamic factors rather than the penetrant size.

Table 8
Thermodynamic parameters for the THF uptake by all the block copolymers

Sample	ΔH^0 (kJ mol^{-1})	$-\Delta S^0$ (Jmol^{-1} K^{-1})	ΔG (kJ mol^{-1})	K_S
(NR/PU)-1	1.2	0.44	2.3	0.116
(NR/PU)-2	0.86	0.87	1.1	0.152
(NR/PU)-3	0.82	0.72	1.04	0.179
(NR/PU)-4	0.76	0.86	1.02	0.191
(NR/PU)-5	0.656	0.86	0.9	0.221

Table 9
E_D, E_P and ΔH_S values for solvent in the THF uptake by all the block copolymers

Sample	E_D (kJ mol^{-1})	E_P (kJ mol^{-1})	ΔH_S
(NR/PU)-1	1.47	4.78	3.31
(NR/PU)-2	1.34	4.60	3.26
(NR/PU)-3	1.22	3.21	1.99
(NR/PU)-4	1.18	2.14	0.96
(NR/PU)-5	1.08	1.3	0.3

The NCO/OH ratio is found to play an important role in the solvent transport. The sorption is found to increase with decrease in the NCO/OH ratio irrespective of the nature of the solvents. However, the mechanism of solvent transport was not affected by this ratio. D^*, S and P values increase with a decrease in NCO/OH. This becomes very significant at the value of 1.26. It seems that at high NCO/OH ratio the excess NCO favours crosslinking in the polymer system through allophanate linkages. The values of 1.26 could be the optimum NCO/OH ratio at which minimum required crosslinking is present in the sample enabling higher level of solvent permeation. Lowering of enthalpy, free energy, E_D and E_P with a decrease in NCO/OH suggests that the polymer–solvent interaction is facilitated at lower values of the NCO/OH ratio.

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