

Elasticity Behavior of Swollen Polyurethane Networks

Da-Kong Lee

Department of Chemical Engineering, National I-Lan Institute of Technology, I-Lan 26015, Taiwan, Republic of China

Abstract: A series of polyurethane networks were prepared by reacting MDI (4,4'-diphenylmethane diisocyanate) with various mixtures of poly(oxyethylene) end-capped poly(oxypropylene) triol and diol. The uniaxial compressive properties of the polyurethane networks both in equilibrium swelling in toluene and in a dried state were measured at 27 °C. The compressive stress-strain data were analyzed according to equations based on the Gaussian theory of elasticity. Deviations from the Gaussian behavior were observed; however, as the polyether diol content increased, deviations from the Gaussian behavior decreased. The interaction parameters between the polyurethane networks and toluene at an equilibrium state were analyzed by the Flory-Huggins equation. As the polyether diol content increased, the interaction parameter, χ , increased due to the increasing content of the poly(oxyethylene) unit and urethane group concentration. With increasing polyether diol content, polyurethane networks approached phantom behavior more closely.

Keywords: Polyurethane networks, Solution behavior, Gaussian behavior, Flory-Huggins equation, Interaction parameter.

Introduction

The efficient utilization of a polymeric material can be achieved only if the structure-property relationships are understood. For elastomeric materials, the most important feature of the molecular structure is the presence of crosslinks leading to a macroscopic, three-dimensional network structure which can be related to the elasticity behavior. The elastomeric networks may be formed by either the crosslinking of high molar weight linear chains or by the end-linking of functionalised monomers and prepolymers. The elasticity behavior of polymer networks can be described by the Gaussian theory [1,2]. Generally, polymer networks exhibit insolubility in any solvent, so the usual solution characterization techniques available for linear polymers can not be used to obtain fundamental molecular information concerning the network structure. However, polymer networks can be swollen to equilibrium in inert solvents and then the polymer network-solvent interaction behavior can be investigated [3-6].

In this paper, a series of amorphous polyurethane networks with different crosslinking density was prepared and the elasticity behavior of these

networks on extension was discussed [7]. In this paper, the stress-strain behavior of these networks in toluene is investigated using uniaxial compression and the results are analyzed using the fundamental rubber elasticity (Gaussian) theory.

Experimental

1. Materials

A poly(oxyethylene) end-capped poly(oxypropylene) polyether triol with a PO/EO weight ratio of 85/15, Propylan M111 (denoted as T), was obtained from Lankro Chemical Ltd. and dried by a rotary film evaporator at 90 °C for 3 hours before use. The equivalent weight, number average molecular weight and water content were determined by acetylation end-group analysis [8], vapor pressure osmometry [9] and Karl-Fischer analysis [10], respectively. The measured values were 2,036 g/mol, 5,627 g/mol and 0.067 wt%, respectively. A poly(oxyethylene) end-capped poly(oxypropylene) polyether diol with a PO/EO weight ratio of 70/30, Niax 1256 (denoted as D), was supplied by Union Carbide. The same treatment was carried out before use. The measured values of equivalent weight, num-

ber average molecular weight and water content were 999 g/mol, 1,978 g/mol and 0.03 wt%, respectively. Flake MDI (4,4'-diphenylmethane diisocyanate), a white crystalline solid at room temperature with a functionality of 2.0. MDI, has a tendency to dimerize at room temperature, and hot-sintering is required to eliminate any MDI dimer or other impurities insoluble in molten MDI [11]. After hot-sintering and filtering, MDI was cooled rapidly and placed in a sealed bottle and stored in a refrigerator at -30 °C. The equivalent weight of the purified MDI was determined by a di-*n*-butylamine back titration method [12] to be 125.0 g/mol.

2. Sample preparation

The polyurethane materials were prepared through a one-shot, hand-cast bulk polymerization process by reacting polyol mixtures with MDI with equal stoichiometric ratios of hydroxyl to isocyanate groups. A typical example was prepared as follows: 10.25 g (0.082 equivalent) of MDI, 100 g (0.049 equivalent) of T and 32.71 g (0.033 equivalent) of D were thoroughly mixed and reacted at 50 °C for 10 minutes. The reaction mixtures were molded and then heated at 100 °C for 1 hour. After demolding, the samples were heated at 100 °C for 3.5 hours and then at 150 °C for a further 1.5 hours to ensure thorough reaction. This polyurethane was denoted as 60T-0; the first part indicates that the content of T in the polyether polyols was 60 equivalent % and the second number indicates that no chain extender was used. The polyurethane samples were immersed in toluene and swelled for several weeks until constant weight was achieved to obtain equilibrium swollen polyurethane networks. The swollen samples were very soft due to a high degree of swelling (600% to 800%) and careful sample handling was necessary to prevent cracking. The equilibrium swollen polyurethane networks were dried very slowly at room temperature for three to four weeks. The term "dried state" is used to describe the completely dried sample (completely free of any sol-fraction).

3. Compression stress-strain measurements

A specially designed uniaxial compression apparatus was used as described by Fasina and Stepto [4]. The compressive stress-strain curves of the polyurethane network specimens in the equilibrium swollen and dried states were measured on cylindrical samples (10 mm diameter and 10 mm height) in a thermostatted room at 27 °C, with the compressive forces in the range of 0 to 15 N, producing deflection in the range of 0 to 3.5 mm. For all the polyurethane networks, three specimens were tested in each state to give the average compressive stress-

Table I. Dimensional data and sol fraction of the polyurethane networks.

Material	ρ (g/cm ³)	V_d/V_f	$\phi_2 (=V_d/V_s)$	Sol fraction (wt%)
100T-0	1.066	0.9754	0.1330	0.98
80T-0	1.072	0.9850	0.1415	1.05
60T-0	1.079	0.9548	0.1488	1.49
40T-0	1.081	0.9428	0.1595	1.95
20T-0	1.111	0.7942	0.1450	9.82
100D-0	1.136	— ^(a)	— ^(a)	— ^(a)

(a) Soluble

strain data.

Results and Discussion

Six amorphous polyurethanes, 100T-0, 80T-0, 60T-0, 40T-0, 20T-0 and 100D-0 with content of polyether triol (T) in the polyols (T and D) of 100, 80, 60, 40, 20 and 0 equivalent %, respectively, were prepared.

The dimensions of the polyurethane networks changed significantly after equilibrium swelling and drying. The density of as-made specimens, ρ , the ratio of the volume in the dried state (V_d) to the volume of as-made specimens (V_f), V_d/V_f , the ratio of the volume in the dried state to the volume in the equilibrium swollen state (V_s), $\phi_2 = V_d/V_s$, and the sol fraction are shown in Table I. It can be seen that the sol-fraction increases with increasing polyether diol content; this result is due primarily to the decreasing in crosslinking density as described by Dušek [1]. For the 20T-0 network, the unexpectedly high sol-fraction is due to the high content of polyether diol. The 100D-0 network is linear (functionality; $f_n = 1.98$) and dissolved in toluene completely.

The uniaxial compression stress-strain data were analyzed according to the equations based on the Gaussian theory [5] of rubber elasticity.

$$\sigma = G_c \left(\Lambda - \frac{1}{\Lambda^2} \right) \quad (1)$$

and

$$G_c = \frac{A_f \rho R T \phi_2^{1/3} (V_d / V_f)^{2/3}}{M_c} \quad (2)$$

thus

$$\frac{M_c}{A_f} = \frac{\rho R T \phi_2^{1/3} (V_d / V_f)^{2/3}}{G_c} \quad (3)$$

where σ is the applied stress, Λ is the deformation

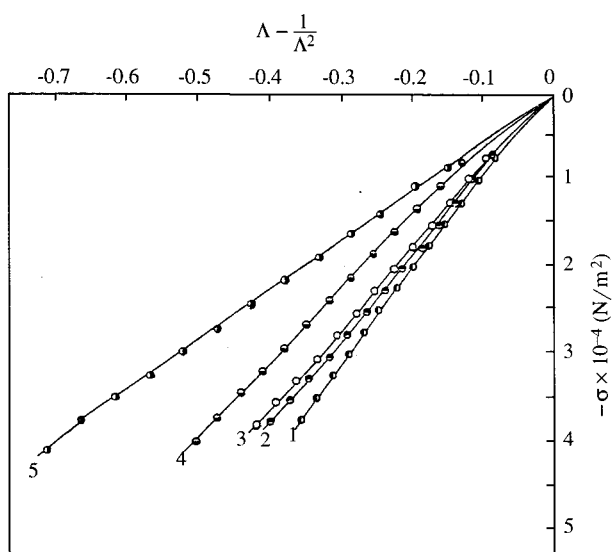


Figure 1. Gaussian stress-strain plots for equilibrium swollen polyurethane networks: (1) 100T-0, (2) 80T-0, (3) 60T-0, (4) 40T-0 and (5) 20T-0.

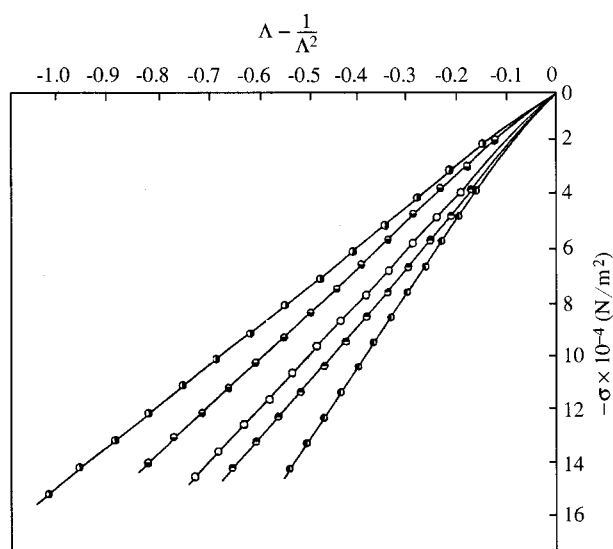


Figure 2. Gaussian stress-strain plots for dried polyurethane networks: (1) 100T-0, (2) 80T-0, (3) 60T-0, (4) 40T-0 and (5) 20T-0.

ratio, $\Lambda = h/h_0$, ρ , is the density of the network, R is the gas constant, T is absolute temperature, $\phi_2 = V_d/V_s$, and M_c is the molar mass between junction points. A_f is a structure factor accounting for the functionality, f , of the network. In the absence of free chain-ends, A_f has a value of $(1-2/f)$ for phantom networks and a value of unity for affine networks [6,13]. The volume of the network at formation is V_f , and V_d is the volume of the dried network.

The Gaussian plots, σ , versus $[\Lambda - (1/\Lambda^2)]$, of the polyurethane networks in the equilibrium swollen and dried states are shown in Figures 1 and 2

Table II. Treated uniaxial compressive stress-strain data of the equilibrium swollen (S) and dried (D) polyurethane networks.

Material	G_0 (MPa)	% error (%)	Δh (mm)	G_0' (MPa)	% error ' (%)	M_c/A_f (g/mol)
100T-0 (S)	0.094	13.5	0.06	0.099	7.6	13,400
100T-0 (D)	0.246	10.5	0.03	0.254	6.2	10,300
80T-0 (S)	0.089	14.9	0.07	0.093	7.0	14,700
80T-0 (D)	0.211	9.7	0.04	0.219	4.8	12,100
60T-0 (S)	0.082	13.5	0.08	0.087	7.7	15,600
60T-0 (D)	0.196	8.7	0.04	0.201	3.6	13,000
40T-0 (S)	0.072	12.0	0.09	0.076	11.1	18,100
40T-0 (D)	0.165	8.8	0.04	0.170	4.2	15,200
20T-0 (S)	0.053	10.9	0.10	0.055	3.2	21,000
20T-0 (D)	0.145	8.0	0.05	0.148	3.3	16,100

respectively. These Gaussian plots should be linear through the origin [$\sigma = 0, \Lambda - (1/\Lambda^2) = 0$]. All plots of σ versus $[\Lambda - (1/\Lambda^2)]$ showed some curvature toward the σ -axis at very small compressive strains, e.g. $[\Lambda - (1/\Lambda^2)] > -0.1$. At higher strains, when $[\Lambda - (1/\Lambda^2)] < -0.1$, the plots become linear. Thus, deviation through the origin is observed. The plots of each network were analyzed in the following ways:

- (1) The slope of the least-squares line through the origin was found, to give G_0 , and the deviation of a plot from linearity was evaluated in terms of the mean |% error|, averaged over all the experimental σ versus $[\Lambda - (1/\Lambda^2)]$ data points [14].
- (2) Surface imperfections and uncertainty on a cylindrical specimen could reduce the cross-sectional area to be subjected to stress in the initial stages of compression. The effects of these factors on the deviation of a Gaussian plot from linearity could be determined by correcting Λ , assuming the specimen had some effective initial height, h_c , which was less than the actual height, h_0 . The value of h_c was determined, which minimized the value of the mean percentage error of the experimental points from the linear least-squares fit through the origin. This is designated as |% error|', and the slope of the line is denoted G_0' [2].

The values of |% error| and |% error|' can be used to quantify deviations from Gaussian stress-strain behavior for these polyurethane networks. Such rubbery networks have been prepared to represent the idealized soft-segment phase in the segmented copolyurethanes.

Table II lists the shear modulus G_0 and the corresponding |% error| using least-squares analysis on all uncorrected data points, G_0' and corresponding |% error|' using least-squares analysis on data modified with initial height correction, and M_c/A_f corresponding to G_0' using Eq.(3) for the polyure-

Table III. ϕ_2 , G_o' , χ of the individual equilibrium swollen sample, $\bar{\chi}^{(a)}$ and the urethane bond concentration of the equilibrium swollen networks based on affine network behavior.

Sample	ϕ_2	G_o' (MPa)	χ	$\bar{\chi}^{(a)}$	$[-NHCOO-]$ (mol/Kg)
100T-0-1	0.1286	0.0974	0.4638		
100T-0-2	0.1337	0.0976	0.4460	0.4438	0.463
100T-0-3	0.1368	0.1004	0.4486		
80T-0-1	0.1390	0.0917	0.4610		
80T-0-2	0.1405	0.0927	0.4623	0.4635	0.512
80T-0-3	0.1437	0.0948	0.4652		
60T-0-1	0.1478	0.0900	0.4771		
60T-0-2	0.1465	0.0869	0.4765	0.4795	0.572
60T-0-3	0.1513	0.0844	0.4850		
40T-0-1	0.1586	0.0781	0.5032		
40T-0-2	0.1567	0.0766	0.4979	0.5015	0.650
40T-0-3	0.1611	0.0764	0.5029		
20T-0-1	0.1455	0.0555	0.5038		
20T-0-2	0.1402	0.0536	0.4999	0.5037	0.751
20T-0-3	0.1484	0.0562	0.4981		

(a) $\bar{\chi}$ is calculated from the average values of ϕ_2 and G_o' .

thane networks. It can be seen that |% error| decreases as polyether diol content increases (M_c/A_f increases) for both equilibrium and dried polyurethane networks. Previous data on polyurethane networks derived from polyester polyols [4] showed a similar trend. The dried polyurethane networks tend to exhibit smaller |% error|. The G_o' values are used here to determine the M_c/A_f according to Eq.(3). As polyether diol content increases, the chemical functionality, f , decreases, G_o' decreases, and M_c/A_f increases, as expected.

The M_c/A_f values of the equilibrium swollen polyurethane networks can be used to interpret more clearly aspects of the solution behavior of the networks in equilibrium swelling experiments. The swelling behavior is investigated using the Flory-Huggins equation [15] for a network which behaves affinely ($A_f = 1$) in a solvent at equilibrium. The swelling equation is given as:

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + (\rho V_1 / M_c)(\phi_2^{1/3} - \phi_2/2) = 0 \quad (4)$$

where χ is the interaction parameter between polymer network chains and solvent, ρ is the network density, V_1 is the molar volume of the swelling solvent (for toluene, $V_1 = 1.06 \times 10^{-4}$ m³/mol at 27 °C), and other terms are described above. χ is a dimensionless parameter which is given by the interaction energy per solvent molecule divided by kT , where k is Boltzmann's constant and T is the absolute temperature. The expression kT therefore represents the difference in energy between a solvent

Table IV. Experimental data and calculated χ values for equilibrium swollen polyurethane networks based on phantom network behavior.

Material	f	F_ϕ	ϕ_2	V_{2c}	$G'(s)$ (MPa)	χ
100T-0	2.76	0.275	0.133	0.975	0.099	0.522
80T-0	2.56	0.219	0.142	0.985	0.093	0.534
60T-0	2.38	0.160	0.145	0.955	0.087	0.544
40T-0	2.23	0.103	0.160	0.943	0.076	0.555
20T-0	2.10	0.048	0.145	0.794	0.055	0.552

molecule immersed in pure polymer ($\phi_2 = 1$) and a solvent molecule immersed in pure solvent. Rearranging Eq.(4) gives

$$\chi = \frac{-[(\rho V_1 / M_c)(\phi_2^{1/3} - \phi_2/2) + \ln(1 - \phi_2) + \phi_2]}{\phi_2^2} \quad (5)$$

χ is calculated according to Eq.(5) for three individual equilibrium swollen samples (i.e., 40T-0-1, 40T-0-2 and 40-T0-3), and the results are summarized in Table III.

All networks' ϕ_2 values are less than 0.16 (i.e., high degree of swelling, $1/\phi_2$), showing toluene to be a good solvent for these polyurethane networks. ϕ_2 increases as the polyether diol content increases except for the 20T-0 network. The M_c/A value of the 20T-0 network used to calculate χ are much greater than those of the other networks and inconsistent with those of the other networks in the series (as demonstrated by the σ versus $[\Lambda - (1/\Lambda^2)]$ plots in Figure 1). This also explains why the swelling of 20T-0 homopolyurethane networks is excessive and thus the ϕ_2 value in Table IV is lower than that expected considering the increasing trend in the other networks. The increase in the $1/\phi_2$ value of 20T-0 may possibly be due to the fact that network 40T-0 reached the critical value of $\chi = 0.5$ [15].

It can be seen that $\bar{\chi}$ increases from about 0.444 to 0.504 as the polyether diol content increases. Two factors may contribute to this. First, higher poly(oxyethylene), POE, content in the polyether diol (POE content in polyether diol and triol to be 30 and 15 wt%, respectively) may decrease the interaction between the network and non-polar solvent (toluene) [16-18]. Second, as the polyether diol content increases, the urethane group concentration, $[-NHCOO-]$, increases (see Table III), and the interaction increases [17]. In polyurethane networks the interaction between molecules causes the "bundle" structure. It was first proposed by Blokland [19], who explained it as the hydrogen bonding between urethane groups and polyether oxygen groups,

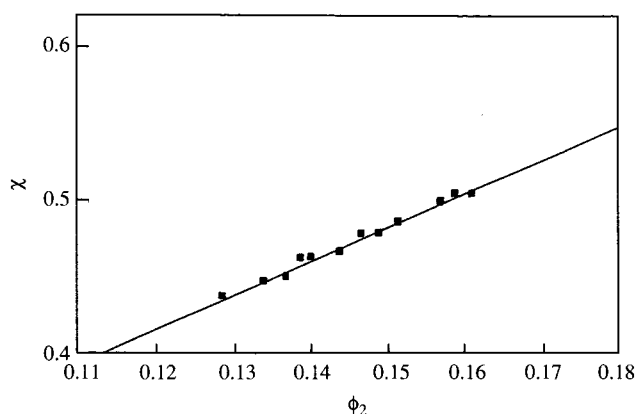


Figure 3. Plots of interaction parameter, χ , versus ϕ_2 for equilibrium swollen polyurethane networks based on affine network behavior.

whereas Dušek [20] later explained it as the bonding between urethane and the urethane groups. Thus, χ increases as the polyether diol content increases.

The higher χ values observed for networks containing higher POE contents are consistent with similar data reported by Lakhanapal et al. [16]. For the polymer solution behavior of linear poly(oxypropylene) (POP)/benzene and POE/benzene systems, at equivalent ϕ_2 values, Booth and Devoy [18] have obtained higher χ values for the POE systems; these results were explained in terms of the lower solubility of POE in non-polar solvents (paraffin, hydrocarbons).

The plot of χ versus ϕ_2 for the equilibrium swollen polyurethane network sample with polyether diol of 60 equivalent % or less is shown in Figure 3. The increasing trend of χ with ϕ_2 follows the general polymer-solution behavior suggested by Flory et al. [21]. The χ - ϕ_2 data are fitted by least-squares polynomial functions to give Eq.(6) with a deviation as low as 0.24%. This trend is similar to that of the natural rubber/benzene system described by Mark [22].

$$\chi = 0.1772 + 1.8772 \phi_2 + 1.0213 \phi_2^2 \quad (6)$$

In fact, the polymer-solution equilibrium swelling behavior is very complicated. Although significantly affected by crosslink density, solvent polarity, intermolecular reaction and the network-forming reactants, swelling behavior is also affected by dilution, network-forming processes and reactant stoichiometry, as discussed by Stanford and Stepto [17]. The work presented by Flory [23], in which the original swelling equation has been modified, shows the extent to which non-affine deformation occurs on swelling, depending on the looseness with which the crosslinks are embedded within the net-

work structure. This, in turn, depends on both the network structure and its degree of equilibrium swelling. The proposed equation is:

$$\begin{aligned} & \ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 \\ & + (F_\phi \rho V_1 / M_c)(V_{2c}^{2/3} \phi_2^{1/3}) = 0 \end{aligned} \quad (7)$$

where V_{2c} is the volume ratio of dried to as-prepared network, V_d/V_f , and F_ϕ is a factor characterizing the extent to which the deformation in swelling approaches the affine limit [24]. F_ϕ is a function of cycle rank, ξ , of the network, the degree of swelling, $1/\phi_2$, and the number of junctions, n , that is,

$$F_\phi = (1 - 2/f)[1 + (n/\xi)K] \quad (8)$$

The cycle rank of a network is the number of chains which must be cut to reduce the network to cyclic or a tree structure, and K is a function of ϕ_2 . For an ideal network showing phantom behavior, $K = 0$, whereas for affine behavior, $K = 1 - \phi_2^2$.

In the present study, the degree of swelling ($1/\phi_2$) is high for the polyurethane networks', therefore, the exhibition of phantom behavior is expected. Thus, $F_\phi = 1 - 2/f$ and Eq.(7) becomes:

$$\begin{aligned} & \ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 \\ & + [(1 - 2/f) \rho V_1 / M_c](V_{2c}^{2/3} \phi_2^{1/3}) = 0 \end{aligned} \quad (9)$$

Then

$$\chi = \frac{-\{[(1 - 2/f)GV_1 / RT]V_{2c}^{2/3}\phi_2^{1/3} + \ln(1 - \phi_2) + \phi_2\}}{\phi_2^2} \quad (10)$$

Assuming phantom network behavior, χ values have been calculated based on Eq.(10). The results and the corresponding parameters are listed in Table IV. These χ values are higher than those calculated by assuming affine behavior. χ values by assuming phantom behavior also show an increasing trend as the polyether diol content increases.

The elasticity behavior of this series polyurethane networks on extension has also been discussed in previous paper [24].

Conclusion

Compressive stress-strain data were analyzed according to equations based on the Gaussian theory of elasticity. Deviations from Gaussian behavior were observed, indicating that as the polyether diol content increases, deviations from the Gaussian behav-

ior decrease. The interaction parameters between polyurethane networks and toluene at the equilibrium swollen state were analyzed by the Flory-Huggins equation and Flory's modified equation, indicating that as the polyether diol content increases, the interaction parameter value increases. This result can be explained by the increasing content of poly(oxyethylene) unit and urethane group concentration. The increasing of polyether diol content and urethane concentration, the polarity and the intermolecular reaction increased. As the polyether diol content increased the polyurethane networks approached phantom behavior more closely.

References

1. K. Dušek and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).
2. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd Ed., Clarendon Press, Oxford, 1985.
3. J. L. Stanford, R. F. T. Stepto and R. H. Still, *Reaction Injection Moulding and Fast Polymerisation Reactions*, Ed. J. E. Kresta, Plenum Press, London, 1982, p. 31.
4. A. B. Fasina and R. F. T. Stepto, *Makromol. Chem.*, **182**, 2479 (1981).
5. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd Ed., Clarendon Press, Oxford, 1985.
6. P. J. Flory, *Proc. R. Soc., London, Ser. A*, **351**, 351 (1976).
7. D. K. Lee, H. B. Tsai and J. L. Stanford, *Polym. Networks Blends*, **7**, 53 (1997).
8. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience Publishers, New York, 1961.
9. J. M. G. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, Intertext Book, London, 1973.
10. D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes*, Vol. XVI, Part 3, Wiley-Interscience, New York, 1965.
11. K. C. Frisch, *Polyurethane Technology*, Ed. P. F. Bruins, Interscience Publishers, New York, 1979, p.1.
12. S. Siggia and J. G. Hanna, *Industrial and Eng. Chem., Anal. Ed.*, **20**, 1048 (1948).
13. J. E. Mark, *Adv. Polym. Sci.*, **44**, 1 (1982).
14. F. P. Wolf, *Polymer*, **13**, 347 (1972).
15. P. J. Flory, *Principles of Polymer Chemistry*, Ithaca, New York, 1953.
16. M. L. Lakhanpal, H. G. Singh and S. C. Sharma, *Indian J. Chem.*, **6**, 2 (1986).
17. J. L. Stanford and R. F. T. Stepto, *Brit. Polym. J.*, **9**, 124 (1977).
18. C. Booth and C. J. Devoy, *Polymer*, **12**, 309 (1971).
19. R. Blokland, *Elasticity and Structure of Polyurethane Networks*, Rotterdam Univ. Pers., 1968.
20. K. Dusek and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).
21. B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, **64**, 2035 (1968).
22. P. J. Queslel and J. E. Mark, *Eur. Polym. J.*, **22**, 273 (1986).
23. P. J. Flory, *Macromolecules*, **12**, 119 (1979).
24. P. J. Queslel and J. E. Mark, *Adv. Polym. Sci.*, **65**, 136 (1984).