Macromol. Symp. ***171,*** *105–114 (2001)*

Formation, Structure and Physical Properties of Ordered Polyurethane Networks

Michal Ilavský[1,2], Helena Valentová[1], Zdĕnka Sedláková[2], Jan Nedbal[1]

[1]Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

[2]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

SUMMARY: The thermal and dynamic mechanical behaviour of ordered stoichiometric as well as off-stoichiometric polyurethane networks based on mesogenic diol - 6,6′-[ethylenebis(1,4-phenyleneoxy)]dihexanol (D), 2(4)-methyl-1,3-phenylene diisocyanate (DI) and poly(oxypropylene) triol (T) is reviewed. The effects of various initial molar ratios of the reactive groups ($[OH]_T/[NCO]_{DI}/[OH]_D$) and of the ordered or isotropic state of the diol on the critical gel structure at the sol-gel transition and a power-law mechanical behaviour is discussed. The effects of amount of mesogenic diol in the elastically active network chains (EANCs) on the conformational rearrangements required for ordering, the concentration of permanent physical interactions (trapped entanglements) and on the intensity of the slow relaxation process in the rubbery region are shown.

Introduction

Polyurethanes of various chemical composition and morphology with amorphous, semicrystalline or liquid-crystalline structures have been studied.[1)] The introduction of a stiff mesogenic group into either the diol or diisocyanate together with flexible spacers generally leads to polyurethanes with thermotropic liquid-crystalline (LC) properties.[2)] In recent years, an increasing interest in LC networks (LCNs) can be observed in the literature.[3-5)] It is found[3,6)] that LCNs in the isotropic state display mechanical behaviour of conventional rubbers whereas in the LC state, a more complex mechanical behaviour, reflecting the coupled response of the mesogenic groups to an applied force, is observed. While the thermal and mechanical behaviour of LCNs has been widely investigated, less attention has been devoted to the network formation process.

In polyurethane systems prepared from polyisocyanates and polyols by the reaction of isocyanate (NCO) and hydroxyl (OH) groups (as well as in other end-linked systems), there are two ways of reaching the gel point (GP), where an infinite structure is first formed.

CCC 1022-1360/00/$ 17.50+.50/0

Generally, the reaction can proceed at various initial ratios of the reactive groups, r_{OH} = [OH]/[NCO]. The increase in conversion at a constant composition of the reacting system (r_{OH} = const) is the first, classic way of reaching the GP at critical conversion of hydroxy, α_{OH}^{c}, or isocyanate, $\alpha_{\mathrm{NCO}}^{c}$, groups ($\alpha_{\mathrm{OH}} \cdot r_{\mathrm{OH}} = \alpha_{\mathrm{NCO}}$). The second way of reaching the GP is the critical molar ratio (CMR) method,[7] consisting in finding the critical initial ratio of the reactive groups, r_{OH}^{c}, (i.e., finding the critical composition) at which the GP occurs just when the conversion of minority groups reaches 100%. Such systems, reacted to full conversion of minority groups, are structurally stable and can be studied over a wide temperature range.

In recent years, it has been demonstrated that the GP can be determined from dynamic mechanical measurements.[9] For the critical gel structure (CG) at the GP, a power-law rheological behaviour was observed, for which the frequency dependences of the storage, G', and the loss, G'', shear moduli at GP are related by[9]

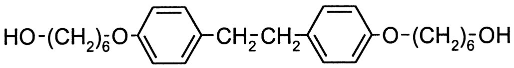
$$G'(\omega) = G''(\omega)/\mathrm{tg}\,\delta = S\,\omega^{n}\,\Gamma(1-n)\cos\delta \qquad (1)$$

where tg δ is the loss tangent (tg $\delta = G''/G'$), $\Gamma(1-n)$ is the gamma function, S (Pa.s^{n}) is the gel strength. $S = G_{0}\tau_{0}^{n}$, where the modulus, G_{0}, and relaxation time, τ_{0}, are material parameters,[9] ω is the angular rate and n is the relaxation exponent. The loss tangent is independent of frequency at the GP and n can be calculated as $n = 2\delta/\pi$. The validity of Eq. (1) is the consequence of structural self-similarity of CG structure and was established for various chemical and physical gelation systems.[8-10]

In this contribution, we summarize the effects of various contents of mesogens in the network chains on the network formation process, the critical gel structure at the GP and the thermal and dynamic mechanical behaviour of fully cured stoichiometric[11] as well as off-stoichiometric networks prepared from a triol (T), diisocyanate (DI) and mesogenic diol (D).

Experimental Part

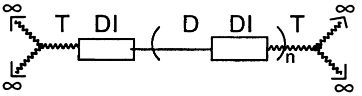
Preparation of Samples: Mesogenic diol, 6,6′-[ethylenebis(1,4-phenyleneoxy)]dihexanol (D)



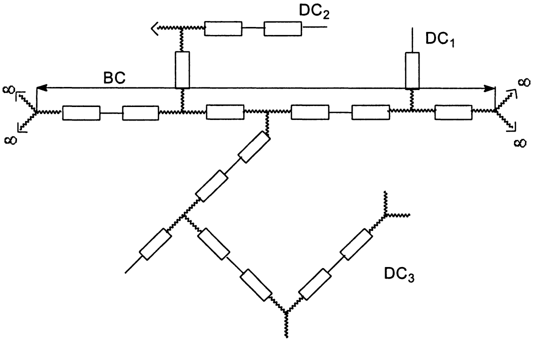
(D)

together with poly(oxypropylene)triol (T, Arcol 420, ARCO Chemical, M_n = 420) and 2(4)-methyl-1,3-phenylene diisocyanate (D) was used for sample preparation.[11]

The stoichiometric networks were prepared at the ratio of the reactive groups ($[OH]_T+[OH]_D$)/ $[NCO]_{DI}=1$ but with various initial molar ratios: $[OH]_T/[NCO]_{DI}/[OH]_D$=1/1/0, 1/2/1, 1/4/3, 1/8/7, 1/12/11, 1/18/17, 1/24/23, and 1/40/39. For comparison, linear polymer with the ratio 0/1/1 was also prepared. In the case of ideal crosslinking, the elastically active network chains (EANC) have the form:



where on average n = 0, 1, 3, 7, 11, 17, 23, and 39 (the molecular weights of the EANCs are M_c = 454, 1045, 2226, 4588, 6951, 10 495, 14 038, and 23 488).



Off-stoichiometric samples were prepared at initial molar ratios of the reactive groups $[OH]_T/[NCO]_{DI}/[OH]_D$ ranging from 1/10/9 to 5/10/9; the ratio of $[NCO]_{DI}/[OH]_D$ = 10/9 was constant for all samples. A series of soluble samples before the GP as well as insoluble networks after the GP were obtained. In off-stoichiometric networks, structures with many dangling chains (DC) on the backbone chain (BC) of an EANC are formed (see structure shown above).

Rheological and Thermal Measurements: Dynamic mechanical behaviour was measured with a Rheometrics SYS-4 in the parallel-plate geometry. The real, G', and imaginary, G'', components of the complex modulus, G^*, and tg δ were determined. Three types of experiments were carried out: a) the isothermal curing reaction was followed in the rheometer at angular rates ω = 1-100 rad s^{-1}; a series of frequency sweeps (one run taking 90 s) during curing was collected; b) cured samples were measured at various constant temperatures; ω varied from 10^{-1} to 10^2 rad s^{-1} and the temperature interval was from 30 to 180°C; c) the temperature dependences of G' and G'' at a constant frequency, f = 1 Hz, on cooling from the isotropic melt and subsequent heating scans in the range from 30 to 160°C (heating and cooling rates ±2°C/min) were also investigated.

Thermal properties were investigated using a Perkin-Elmer DSC-2 calorimeter and data were collected over cooling and subsequent heating scans (cooling and heating rate ±10 K min^{-1}). A polarizing optical microscope (Photomikroskop III, Zeiss-Opton, crossed polarizers) equipped with a Mettler FP5/FP52 heating stage was used for the texture investigation (cooling and heating rates varied between 10 K min^{-1} and 3 K min^{-1}). Wide-angle X-ray patterns were taken using an HZG4A diffractometer (Freiberger Präzisionsmechanik, Germany) using Ni-filtered CuKα radiation. A heating chamber was attached to the instrument.

Results and Discussion

Diol and Linear Polyurethane

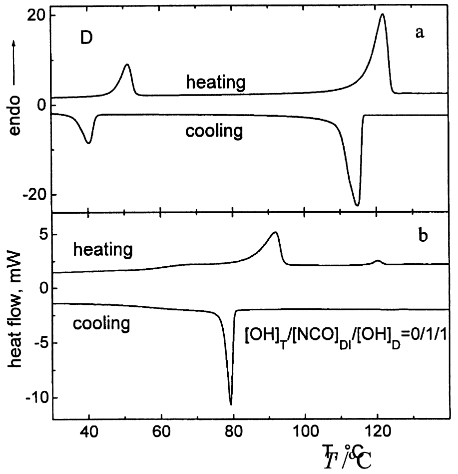


Fig. 1: DSC traces of mesogenic diol D (a), and linear polyurethane (0/1/1) (b); traces on cooling the melt and in the second heating run.

Fig. 1 shows the DSC thermograms of diol D and linear sample with the ratio 0/1/1. On cooling the isotropic melt and in the second heating run, two transitions can be observed for D (Fig. 1a); as expected, the transition temperatures on heating are about 10°C higher than those on cooling. X-ray measurements showed[12)] that the transition located at the lower temperature is a crystal/crystal transition. It was proved that the low-temperature crystalline modification cannot be transformed into the high-temperature one by annealing.

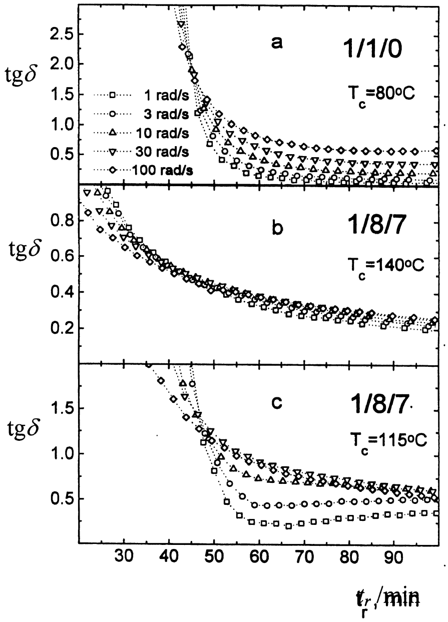


Fig. 2: Dependence of the loss tangent, tg *δ*, on reaction time t_r for two networks with ratios *r* = 1/1/0 and 1/8/7 at the indicated curing temperatures, T_c.

From Fig. 1b, cooling of the isotropic melt of linear sample 0/1/1 leads to the formation of a mesophase at ≈ 80 °C, which is subsequently frozen-in below the glass-transition temperature $T_g \approx 57$ °C. This mesomorphic glass showed, by X-ray and polarizing microscopy, a nematic texture.12) Optical microscopy and X-ray scattering measurements have revealed that, after melting the nematic phase, a new, better-ordered, probably smectic structure forms up between 95 and 115 °C. This structure melts at ≈125 °C.

Stoichiometric Networks

Critical Gel: Fig. 2 shows an example of the evolution of tg δ at five constant frequencies as a function of reaction time t_r for two samples with the ratios 1/1/0 and 1/8/7. For the amorphous 1/1/0 system cured at T_c = 80 °C (Fig. 2a), the crossover of tg δ occurs at tg δ = 1.8; the corresponding gel point time t_g = 45 min and the value of the relaxation exponent n = 0.68. Exponents between 0.5 and 0.7 were found earlier for similar chemically crosslinked polyurethane systems.8-10)

Fig. 2b shows an example of the evolution of tg δ with time t_r for the 1/8/7 sample cured in the isotropic state at T_c = 140°C; the crossover occurs at tg δ_i = 0.5 and the isotropic relaxation exponent n_i = 0.3. The same mixture was also cured in the ordered state of D at

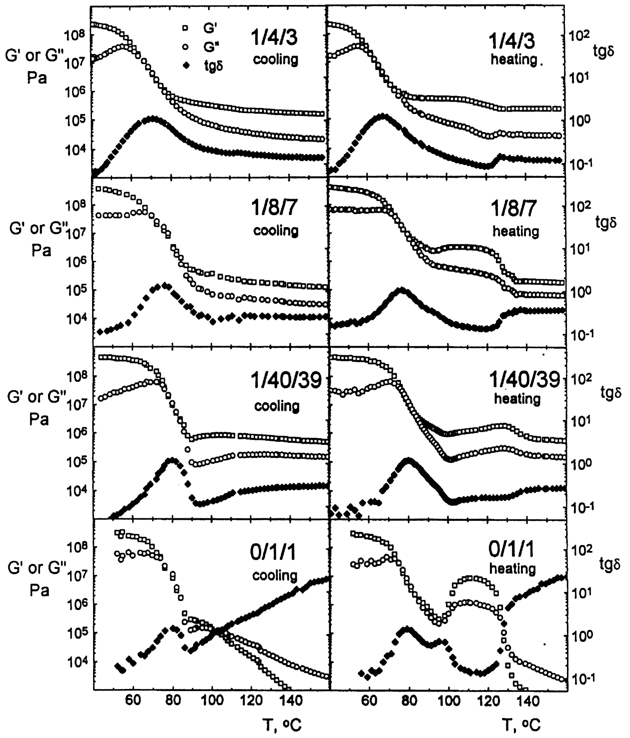


Fig. 3: Temperature dependencies of the storage, G′, and loss G″ moduli, and the loss tangent, tg δ (measured at 1Hz) for samples with the indicated ratios of reactive groups $[OH]_T/[NCO]_{DI}/[OH]_D$

state of D at 115 °C (Fig. 2c). X-ray measurements[11)] revealed a smectic texture in this sample after curing and quenching the sample to room temperature (no such structure was found for a quenched sample reacted at 140 °C). In the former case, the crossover tg δ_{LC} = 1.25, giving n_{LC} = 0.57. Higher n_{LC} than n_i values were observed for all samples with mesogenic diol D. As was pointed out earlier,[9-10)] the values of the critical gel parameters n and S depend on the structure of the reactants and the type of crosslinking reaction. Our results show that these parameters also depend on whether curing takes place in the isotropic or ordered state. This is due to the fact that in the ordered state, the critical gel is formed by chemical bonds together with strong physical interactions originating in mesophase domains. In such way, the aggregation of mesogens enhances the connectivity of the molecular structure at the GP.

Viscoelastic Behaviour: Temperature dependences of moduli G' and G'' and tg δ of selected samples measured at a frequency f = 1 Hz obtained on cooling from 160 °C and subsequent a ±2 °C min^{-1} heating scan rate, are shown in Fig. 3 together with the data for linear sample 0/1/1. Fig. 3 clearly demonstrates that the mechanical behaviour of ordered networks is dependent on the molecular weight of the EANCs (or amount of diol D in an EANC), especially in the rubbery region. In particular, the network-forming process introduces junction points that reduce the flexibility of the chain between junctions and inhibit the conformational rearrangements required for ordering. The increase in G' and G'' in the rubbery region observed in heating scans decreases with decreasing diol content in the EANC. Experimental values of storage moduli measured in the isotropic state at 150 °C, G'_{150}, can be compared with those expected from the structure. If we consider the rubber elasticity model with a trapped entanglement contribution, we can write[13)]

$$G'_{150}/RT = A\nu_e + \Delta \qquad (2)$$

where R is the gas constant, T = 423 K, A is the front factor[14)] ($A = (f_e-2)/f_e = 1/3$ for the phantom network model and A = 1 for the affine network model, respectively), ν_e is the chemical concentration of EANCs and Δ is the entanglement contribution (permanent physical interaction contribution). The value of Δ was calculated for the phantom limit (A = 1/3) and an ideal crosslinking process

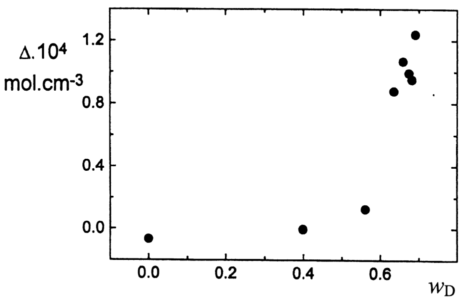


Fig. 4: Dependence of trapped entanglement contribution Δ on the weight fraction of mesogenic diol, w_D

($\nu_e = \rho/M_c$), from Eq. (2): $\Delta = G'_{150}/RT - \rho/(3M_c)$ ($\rho = 1.13$ g cm^{-3} is the density). Fig. 4 shows the dependence of Δ on the weight fraction of the diol in the EANC, w_D. While for low w_D values, the parameter $\Delta \cong 0$, with increasing w_D, the Δ values strongly increase. Usually the opposite dependence of the entanglement contribution Δ on concentration of EANCs is observed in amorphous networks.[10)] In such way, the value of modulus in the isotropic rubbery state is affected by the strong interchain interactions between mesogenic groups and the extent of these interactions increases with increasing content of mesogenic diol in the EANC.

Off-Stoichiometric Systems

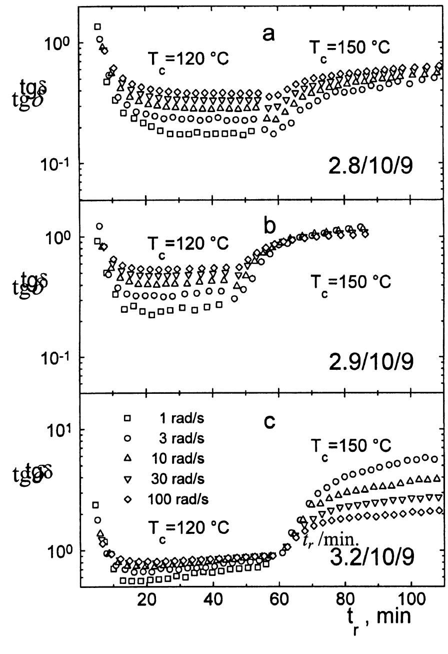


Fig. 5: Dependence of the loss tangent, tg δ, on reaction time, t_r, for three samples near the CG state at the indicated curing temperatures T_c.

Critical Gel: Initially curing was carried out in all cases at T_c = 120 °C (in the ordered state of diol). After reaching constant values of tg δ with respect to curing time t_r (t_r = 60 min), the temperature was raised to 150 °C and the curing reaction was again investigated. An example of the evolution of tg δ at T_c = 120 and 150 °C for three samples near the critical GP ratio of reactive groups is shown in Fig. 5. In all cases, the crossover of the tg δ can be seen at short $t_c \approx 7$ min at T_c = 120 °C; a solid-like behaviour with tg $\delta < 1$ appears after this time. For sample 2.8/10/9, a subsequent increase in temperature to T_c = 150 °C is accompanied by an increase in tg δ with curing time t_r; the solid-like behaviour, with tg δ<1, remains (Fig. 5a). On the other hand, after an increase in temperature to T_c = 150 °C, for sample 2.9/10/9, an increase in tg δ with t_r is observed and tg δ becomes virtually independent of ω (Fig. 5b, tg $\delta \approx 1$), characteristic of the CG state (see Eq. (1)). Fig. 5c shows evolution of tg δ with time t_r; for the 3.2/10/9 sample; after an increase in temperature to T_c = 150 °C, a liquid-like behaviour is observed for this sample (tg $\delta > 1$). This facts again suggests that the mesophase formation at T_c = 120 °C enhances the connectivity of the molecular structure at the GP.

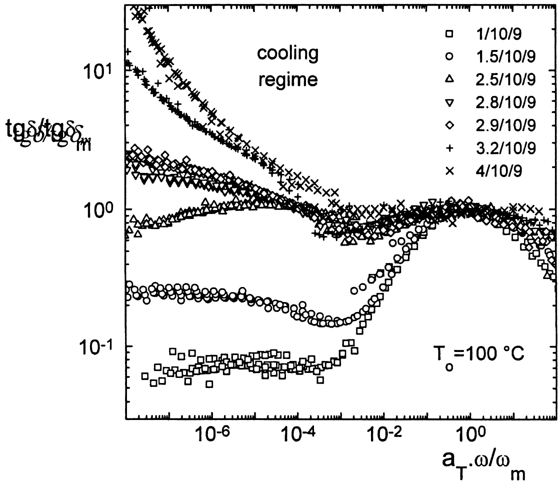


Fig. 6: Dependence of the reduced loss tangent, tg δ/tg δ_m, on reduced frequency $\omega.a_T/\omega_m$ for polymer samples with indicated reactive group ratios $[OH]_T/[NCO]_{DI}/[OH]_D$.

Isothermal frequency scans of G', G'' and tg δ, measured on networks and uncrosslinked systems before the GP in the regime of decreasing temperature (no ordered structures were observed above 90 °C), were superimposed to master curves at reference temperature, T_o = 100 °C. Fig. 6 shows plots of reduced loss tangent tg δ/tg δ_m against the reduced angular rate $a_T\ \omega\ /\omega_m$ (tg δ_m is the value of the maximum of the dependence of tg δ on $a_T\ \omega$; this maximum is located at the frequency ω_m and a_T is the horizontal shift factor). As expected, the narrowest maximum, corresponding to the glass transition, was found for the stoichiometric network 1/10/9; with increasing content of triol in a system, the maximum broadens. Much more pronounced changes in the dependence of tg δ/tg δ_m on $a_T\ \omega\ /\omega_m$ with increasing triol content are found in the rubbery and flow regions. While for uncrosslinked samples, the ratio tg δ/tg δ_m decreases with increasing $a_T\ \omega\ /\omega_m$ (liquid-like behaviour), for networks, tg δ/tg δ_m increases with $a_T\ \omega\ /\omega_m$; in this case, an additional slow relaxation process contributes. A qualitatively similar broadening of the main transition, together with an increasing contribution of the slow relaxation process with decreasing EANC concentration, was also observed for stoichiometric networks. From Fig. 6 it further follows that the CG structure with the 2.9/10/9 ratio exhibits a small decrease in tg δ with increasing $a_T\ \omega\ /\omega_m$ so that the power-law rheological behaviour is not exactly obeyed.

Conclusions

Rheological measurements during the curing in the ordered state of the diol have shown that the critical structure at the GP is formed by chemical junctions as well as strong physical interactions (the mesophase enhances the connectivity of the CG structure). Increasing the concentration of chemical junction points in networks inhibits the conformational rearrangement required for mesophase formation. Strong physical interactions, even in the isotropic state, increase the concentration of trapped entanglements and the intensity of the slow relaxation process in the rubbery region. The off-stoichiometric sample with a CG structure (with the 2.9/10/9 ratios) exhibits a small frequency dependence of the loss tangent in the isotropic state, so that the power-law behaviour is not exactly obeyed.

Acknowledgement

Financial support of the Grant Agency of the Academy of Sciences of the Czech Republic (grant A4112901), the Grant Agency of the Charles University (grant GAUK 46/1998/B) and of the Ministry of Education of the Czech Republic (Project No. MSM 11320001) is gratefully acknowledged.

References

1. K.C. Frisch, D. Klempner: "*Advances in Urethane Science and Technology", Vol. 13*, Technomic Publishing AG, Basel 1996
2. S.M. Aharoni, S.F. Edwards, *Adv. Polym. Sci.,* **118** (1994)
3. K. Hainmerschmidt, H. Finkelmann, *Makromol. Chem.* **190**, 1089 (1989)
4. U. Caruso, B. Panunzi, A. Roviello, A. Sirigu, *Macromolecules* **27**, 3513 (1994)
5. F.J. Davis, G.R. Mitchell, *Polymer* **37**, 1345 (1996)
6. F.J. Davis, A. Gilbert, J. Mann, G.R.J. Mitchell, *J. Polym. Sci.* **A28**, 1455(1990)
7. J. Budinski-Simendić, Z.S. Petrović, M. Ilavský, and K. Dušek, *Polymer,* **34**, 5157 (1993).
8. M. Ilavský, Z. Bubeníková, K. Bouchal, J. Fähnrich, *Polymer* **37**, 3851 (1996)
9. J.C. Scanlan, H.H. Winter, *Macromolecules* **24**, 47 (1991)
10. M. Ilavský in "*Polymer Networks. Principles of Their Formation Structure and Properties"* (R.F.T. Stepto), Blackie Academic and Professional, Chapman and Hall, New York 1998, Chap. 8, p. 243.
11. H. Valentová, K. Bouchal, J. Nedbal, and M. Ilavský, *J. Macromol. Sci., Part B: Polym. Phys.,* **38**, 51 (1999).
12. M. Ilavský, K. Bouchal, H. Valentová, F. Lednický, A. Sikora, and J. Baldrian, *J. Macromol. Sci., Part B: Polym. Phys.,* **37**, 645 (1998).
13. D.S. Pearson, W.W. Graessley, *Macromolecules* **13**, 1001 (1980)
14. P.J. Flory, *J. Chem. Phys.* **66**, 5720 (1977)