Polymer Bulletin 58, 201–211 (2007)
DOI 10.1007/s00289-006-0589-0

Polymer Bulletin

# Effect of diluent on the gel point and mechanical properties of polyurethane networks

**Andrea Ďuračková[a) b)], Helena Valentová[c)], Miroslava Dušková-Smrčková[a) c)] (✉), and Karel Dušek[a)]**

[a)] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6
[b)] Tomas Bata University, Zlín, Czech Republic
[c)] Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, Prague 8, Czech Republic
E-mail: m.duskova@imc.cas.cz; Fax: 00420 296 809 410

Received: 15 July 2005 / Accepted: 15 August 2005

## Summary

Gel point conversions and equilibrium tensile moduli of polyester-based polyurethane networks were determined for different dilutions during network formation. Also, the limiting dilution beyond which the network was not formed at full conversion of functional groups was determined. It ranged between 92 and 94 % of diluent. The scaling dependences against the reference states – the ring-free case and the limiting dilution case - showed that the excluded volume effects were operative and structural changes associated with cyclization affected the rates of both the intramolecular and the intermolecular reactions.

## Introduction

It is known that the presence of diluents during polymer networks formation affects evolution of network structure and network properties [1-3]. First of all, the addition of diluent may induce phase separation during network formation in the form of macro- or microsyneresis [3-6], and facilitate volume phase transition in the final gel [7,8]. However, even in the absence of such changes of state, the effect of a diluent is noticeable compared to a diluent-free system. In the pregel region, the molecular weight averages are lower and the gel points are shifted to higher conversion [2]. Beyond the gel point, lowering of the equilibrium modulus and increase of the sol fraction are the major effects [2,9-11].

Lowering of the *number-average* molecular mass with respect to that expected for the given degree of conversion of groups into bonds can be unequivocally ascribed to ring formation (intramolecular reaction) if there are no other chemical reasons for a change. However, *the mass-average ($M_w$) and higher averages of molecular mass,* as

---

Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks", Prague, 10–14 July 2005 well as the *gel point conversion* depend on the functionality and molecular mass distributions and thus on chemical and physical factors influencing network formation. These factors include reaction mechanism and kinetics (differences and changes in effective group reactivity), diffusion control of the reaction rate, excluded volume, etc. In many cases, cyclization remains apparently one of the major reasons for lowering of $M_w$ and shift of the gel point.

Beyond the gel point, it is the equilibrium modulus which is the most sensitive to the presence of diluent during network formation. The gel part is characterized by large number of cyclic structures (circuits) (cf. the *cycle-rank* in Flory's theory of rubber elasticity), but network chains in only some of them - elastically inactive loops - do not contribute to the equilibrium modulus of the network. Moreover, dilution during network formation weakens the interchain interactions and that is manifested by a decrease in the concentration of the trapped entanglements.

The intensity of cyclization is variable and systems are known where cyclization is negligible in bulk and at moderate dilutions. Examples of such systems are Bisphenol A type polyepoxides crosslinked with some diamines, cf., e.g., Refs. [12, 13]. Vinyl-polyvinyl copolymers formed by free-radical mechanism are the other extremes with prevailing cyclization at the beginning of the crosslinking reaction [14, 15].

In this contribution, we report on the study of gelation and equilibrium elasticity of polyurethane networks from polyester precursors of different functionality and architecture, crosslinked with a trimer of 1,6-diisocyanatohexane.

## Experimental

### *Materials*

Poly(ε-caprolactone) diol (PCLD, $M_n$ = 1250 g/mol) and poly(ε-caprolactone) triols (PCLT, $M_n$ = 300 and 900 g/mol) were supplied by Aldrich. These polymers were dried at 80 °C for 48 h under vacuum. Desmodur N 3300 (trimer of 1,6-diisocyanatohexane) obtained from Bayer A.G. and dibutyltin dilaurate (Fluka) as catalyst were used as received. Diethylene glycol dimethyl-ether (diglyme) and 2-heptanone (Aldrich Co. Ltd) were stored over 4-Å molecular sieves prior use. The tetrafunctional polyester star was sequentially synthesized from pentaerythritol, methylhexahydrophthalic anhydride, and ethylene oxide as described in Ref [16].

### *Determination of OH groups*

About 0.4–0.6 g of polyol was dissolved in 4 ml of *N,N*–dimethylformamide and 4 ml of *N*–methylimidazole as catalyst were added. Then, 5 ml of the acetylation mixture (100 ml of solution in toluene which contained about 11.8 ml of acetic anhydride) was precisely added either to the mixture with polyol or to the same mixture without the polyol (blank experiment). The mixtures were allowed to react for 20 min. at room temperature. After that, 5 ml of water was added. The amount of OH groups was determined by potentiometric titration with 0.5 mol/l solution of KOH in EtOH.

### *Functionality distribution and averages*

The functionality averages were calculated from the hydroxyl content and number-average molar mass determined by VPO. For the PCL polyols, it was assumed the the diol contains mono-ol as admixture, and triol has a diol component as admixture. For determination of functionality distribution of the trimer of 1,6-diisocyanatohexane Desmodur N 3300, the triisocyanate was deactivated first by *n*-butanol or di-*n*-butylamine and the reaction products were separated and determined by Electrospray Ionization FT Mass Spectrometry (ESI-FT-MS) [17]. The functionality averages are expressed as first-moment and second-moment averages defined by

$$\langle f_X \rangle_1 = \sum_{f_X} f_X n_{fX}, \qquad \langle f_X \rangle_2 = \frac{\sum_{f_X} f_X^2 n_{fX}}{\sum_{f_X} f_X n_{fX}} \tag{1}$$

where $n_{fX}$ is the number fraction of molecules having $f_X$ functional groups. The results are given in Table I

**Table I.** Functionality averages of the precursors

| precursor | $\langle f_{OH} \rangle_1$ or $\langle f_{NCO} \rangle_1$ | $\langle f_{OH} \rangle_2$ or $\langle f_{NCO} \rangle_2$ |
|---|---|---|
| PCLD 1250 | 1.87 | 1.93 |
| PCLT 900 | 2.95 | 2.97 |
| PCLT 300 | 2.89 | 2.93 |
| STAR | 3.99 | 4.00 |
| Desmodur 3300 | 3.50 | 3.62 |

### *Analysis of isocyanate groups*

The isocyanate groups in the test portion of the reaction mixture were reacted with excess of di-n-butylamine (solution of 0.2 mol/l in dry THF) at room temperature to form the substituted urea. The excess of amine was than determined by titration with hydrochloric acid (0.1 mol/l), using the bromophenol blue as an indicator.

### *Preparation of samples*

Hydroxy-functional precursors - polycaprolactone diol (PCLD) and triols (PCLT) of different molecular mass - were dissolved in suitable solvents to get 20, 30, 40, 50, 60, 70 and 80 %-wt. solutions. Dibutyltin dilaurate (500 ppm based on solids) as catalyst in 1 % solution in MAK or diglyme and triisocyanate (trimer of 1,6-diisocyanatohexane, Desmodur N 3300) as crosslinker were added. The mixture was stirred approximately for three minutes. The initial molar ratio [NCO] / [OH] was kept equal to one. The solution was poured into a glass mold to make sheets (about 2 mm thick). The samples were kept at room temperature for about 2 days, and later at elevated temperature (50ºC) for 1 day to achieve full conversion of NCO groups. The content of NCO functionalities was confirmed by FTIR ATR test and was below the resolution range of the equipment, i.e below 1 %-wt.

### *Monitoring of reaction between OH and NCO groups - FTIR measurements*

The decrease in the concentration of NCO groups was determined by FTIR spectroscopy. The decrease in the intensities of the stretching band (2273 cm$^{-1}$) was observed during formation of polyurethane network. The intensity of NCO group band was compared with the intensity of the C-H stretching band at 2930 cm$^{-1}$, which remains practically constant during the reaction to ensure independence of the results of the thickness of the sample.

### *Determination of gel point conversion*

The reactants, solvent and catalyst were mixed for about 3 minutes. The material was divided into small portions of approximately 0.5 g and inserted into sealed vials. The vials were kept in the temperature bath. In given time, the solution of di-n-butylamine in THF was added to the reaction mixture to a vial and well stirred into the mixture. A small amount of dichloromethane was added after few seconds to the material in vial. Solubility was assessed by visual examination. The whole procedure was repeated with another vial after certain time. The critical (gel) time was the first time at which insoluble fraction appeared. The critical conversion was determined from the FTIR spectra measured on a control sample of the same reaction mixture.

### *Equilibrium swelling measurement*

The pieces of crosslinked polymer of about 0.1–0.2 g were precisely weighed and put in a sufficient amount of solvent. The volume of solvent was about 50 times larger than the sample volume. Weight of the swollen sample was determined at various time intervals until it was constant. The fractions of sol were determined from the difference of dry samples before and after extraction. The volume fraction of polymer in the swollen sample ($\varphi_2$) is calculated from weights of the swollen ($m_{\mathrm{sw}}$) sample and dry sample after extraction ($m_{\mathrm{d}}$) and specific gravities of the polymer ($\rho_p$) and solvent ($\rho_s$)

$$\varphi_2 = \frac{m_d / \rho_p}{m_d / \rho_p + (m_{sw} - m_d)/\rho_s} \qquad \mathbf{(2)}$$

### *Determination of sol and gel fractions*

The samples of polyurethane network were cut into small pieces and dried to constant weight. The dried pieces were swollen in acetone and dichloromethane. To promote sol extraction, the solvent was 4 –5 times replaced. To determine the fraction of gel and sol in the sample, the extracted material was dried to a constant weight.

### *Rheological measurements and determination of equilibrium moduli*

Rheological behaviour was measured on the Dynamic Mechanical Analyser Tritec 2000 (Triton Technology Ltd.). Fully cured systems, swollen and dry, were studied. Rectangular samples (5 × 1.5 to 3 × 10 mm) were used in fullyclamped bending mode. Frequency dependences of the complex Young modulus $E^* = E' + iE''$ ($E'$ is the storage and $E''$ the loss modulus) were measured in a single cantilever bending mode and at ambient temperature.

Temperature dependencies of dynamic mechanical properties were measured at heating rate 2 °C/min in the temperature range from –60 to 50 °C. Multifrequency mode was used to determine a dependence of $E^*$ on frequency ($f$) at five different frequencies $f$ = 0.31 Hz, 1 Hz, 3.1 Hz, 10 Hz and 31 Hz.

Temperature and frequency measurements were done to ensure that the system is in its rubbery state. For all measured samples, the Young modulus was independent of frequency and *E*" << *E*' at ambient temperature, so that *E*' could be regarded as the equilibrium modulus. From Young modulus *E*, shear modulus was calculated from equation $E = 3G$. Swollen samples were measured in air. During the measurement less than 1 % of the solvent from free standing sample was evaporated.

## Results and Discussion

Since addition of a diluent to crosslinking system promotes cyclization, the structure of the branched polymers before the gel point and of the network is different as shown in Fig. 1.

The ring-free state, where all structures before the gel point are tree-like and there are no elastically inactive loops in the gel, is approached only for a few systems. In a majority of real systems some cyclic "defects" always exist and their formation is promoted by dilution. This is the case of the polyurethane systems discussed here. When dilution further increases, the critical conversion is eventually shifted to 1. This is called *limiting* or *critical* dilution and above this limit only microgel-like products are formed (see also Ref. [11]) and formation of a coherent network is not possible. The critical dilution was found to be 6, 7, and 8 % polymer for PCLD, PCLT 900, and star networks, respectively. This is very interesting: The limiting dilution decreases with increasing functionality of the precursor, although one could expect the reverse – a higher fraction of bonds should be transformed into cycles to make the structures finite and soluble. Increasing compactness of molecules with increasing precursor functionality hindering both inter- and intramolecular reactions is the reason. This is a situation similar to chain crosslinking polymerization characterized by strong initial cyclization and immobilization of pendant C=C double bonds [14-15].

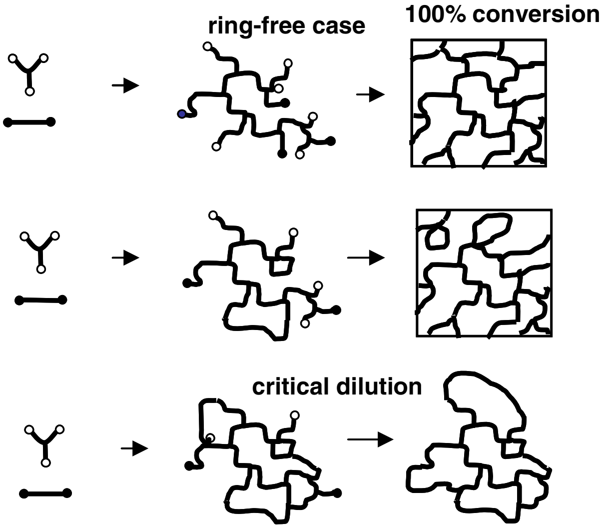


**Figure 1.** Development of branched and network structures in the ring-free case, at moderate cyclization and beyond the critical dilution.

*Gel points*

The shifts of the gel points to higher conversion with increasing dilution is shown in Figs. 2 and 3 as a function of initial molar concentration of functional groups, $c_0$, or its reciprocal value $1/c_0$.

The plot in Fig. 2 includes the whole range of real concentrations and data in Fig. 3 includes a ring free-value of critical conversion, $\alpha_c$, (at $1/c_0 = 0$) calculated from second-moment average functionalities determined experimentally (cf. experimental section).

$$\alpha_c = \left((\langle f_{\mathrm{OH}}\rangle_2 - 1)(\langle f_{\mathrm{NCO}}\rangle_2 - 1)\right)^{-1/2} \qquad \mathbf{(3)}$$

It is seen that the experimental dependence extrapolates fairly well to the value calculated for the ideal ring free-case. Also the limiting dilution values seem to fit a continuous dependence. As expected [2], higher functional systems show up a steeper shift of the gel points to higher conversions.

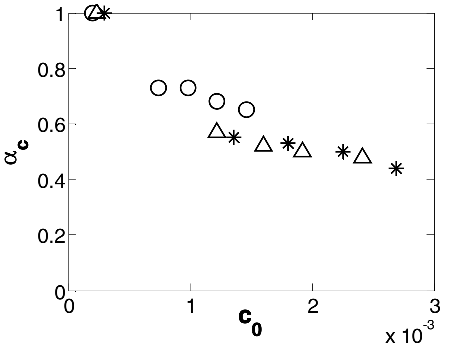


**Figure 2.** Dependence of critical conversion of isocyanate groups on initial concentration of reactive groups, $c_0$ [mol/g]. Systems with poly (ε-caprolactone) diol (○), poly(ε caprolactone) triol 900 (△), and with star (✳).

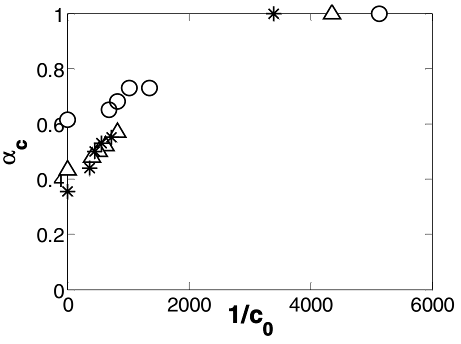


**Figure 3.** Dependence of critical conversion of isocyanate groups on the reciprocal initial concentration of reactive groups, $1/c_0$. Symbols as in Fig 2.

Following the usual consideration, the bonds formed are either intermolecular or ring closing (intramolecular), so that the total conversion of functional groups into bonds is composed of two contributions, an inter- and an intramolecular ones:

$$\alpha_{\mathrm{t}} = \alpha_{\mathrm{inter}} + \alpha_{\mathrm{ring}} \qquad \mathbf{(4)}$$

and, at the gel (critical) point

$$\alpha_{\mathrm{c,t}} = \alpha_{\mathrm{c,inter}} + \alpha_{\mathrm{c,ring}} \qquad \mathbf{(5)}$$

A simple consideration for a second order crosslinking reaction that, ideally, upon dilution the intramolecular reaction rate is proportional to $c_0^2$, whereas cyclization rate to $c_0$ leads to the result that the conversion should be a linear function of reciprocal dilution

$$\alpha_{\mathrm{c,t}} = \alpha_{\mathrm{c,inter}} + P_{ring} / c_0 \qquad \mathbf{(6)}$$

where the factor $P_{\mathrm{ring}}$ is equivalent to the ratio of cyclization to intermolecular crosslinking rate constant. This equation has been applied to various systems and has also been applied here. The linear dependence on $1/c_0$ is based on several assumptions: (1) independence of $P_{\mathrm{ring}}$ of critical conversion and (2) constancy of $\alpha_{\mathrm{c,inter}}$ and equality to Eq. (3), for equal and independent reactivities of functional groups. None of these assumptions is valid at moderate and higher intensities of cyclization. $P_{\mathrm{ring}}$ varies with conversion and is dependent on $c_0$ and $\alpha_{\mathrm{c,inter}}$ is not constant, because the molecules become more compact before the gel point is reached. Thus, the dependence of $\alpha_{\mathrm{c,t}}$ on $1/c_0$ need not be linear and, in fact, non-linearity is often observed. Equation (6) is strictly valid only in the limit of $1/c_0 = 0$, where the probability of cyclization becomes negligible and neither intra- nor intermolecular reactions are affected by existing cycles.

Adhering still to the interpretation given by Eq. (5), the percentages of bonds wasted in cycles at the gel point at volume fraction of polymer during network formation $\varphi_0 = 0.6$ is compared in Table 1.

**Table 1.** Apparent relative extent of cyclization as difference $\alpha_{\mathrm{c,t}}$ - $\alpha_{\mathrm{c,inter}}$

| system | $\alpha_{\mathrm{c\ ring}}/\alpha_{\mathrm{c\ t}}$ [%] |
|---|---|
| PCLD 1250 | 10.5 |
| PCLT 300 | 17.5 |
| PCLT 900 | 16.3 |
| STAR 950 | 28.4 |

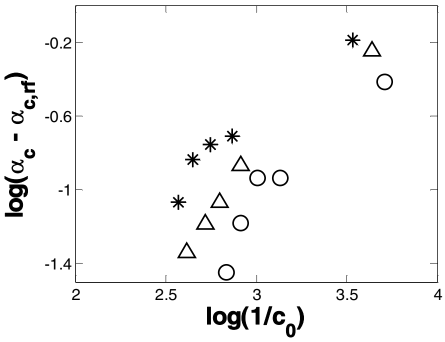
However, the gel point conversion is also affected by excluded volume effect which is at network formation operative due to thermodynamic reasons but mainly due to steric exclusion which makes the effective reactivity of a functional group dependent on the size and branched structure of reacting macromolecules. The effective reactivity of functional groups in large and bulky macromolecules is lower than that in small and "open" molecules. Even more is the effective reactivity affected by ring formation and this concerns both inter- and intramolecular reactions. The molecules with internal cycles are generally stiffer and reactive groups can meet with greater difficulty. The excluded volume has an effect on gel-point conversion. It was observed experimentally by Burchard that the distribution of molecular weights of branched molecules is affected by excluded volume effect [18, 19]. Available are also results of simulation of network development described by Smoluchowski coagulation equation with so-called exponent kernel $K_{xy} \propto l_{Ax}^{\omega} l_{By}^{\omega} + l_{Ay}^{\omega} l_{Bx}^{\omega}$ ($l_{Ax}$ and $l_{By}$ are numbers of functional A-groups in molecule $x$ and B-groups in molecule $y$, respectively), when the exponent $\omega < 1$ [20]. The latter condition imitates the fact that groups hidden inside the molecules are less accessible and thus less reactive and the gel point, without considering cyclization, is shifted to higher conversions.

The conclusion from this qualitative discussion is that $\alpha_{\mathrm{c,ring}}$ expresses the effect of presence of diluent on the critical conversion but the difference $\alpha_{\mathrm{c,t}} - \alpha_{\mathrm{c,inter}}$ only partly reflects the effect of cyclization. It is also affected by changes of rate of intermolecular reaction. Therefore, this and similar quantities should bear the attribute *apparent*.

For further analysis, it is useful to examine the scaling and values of exponents relative to the reference points - ring-free case and limiting dilution state (Figs 4 and 5). Scaling with respect to the ring-free system (Fig. 4)

$$\alpha_{\mathrm{c,t}} - \alpha_{\mathrm{c,inter}} \propto (1/c_0)^{\sigma} \tag{7}$$

gives $\sigma \approx 1.5$. Since cyclization is always taken as relative to intermolecular reaction, the upward curvature probably means that intermolecular reaction is more obstructed by forming cycles than the intramolecular one. Whether this is a more general trend should by examined for more systems. Scaling with respect to the state of limiting dilution (Fig. 5)



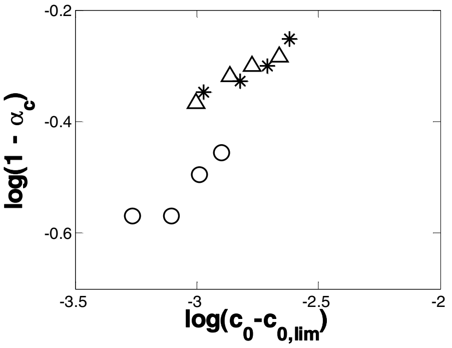


**Figure 4.** Log-log plot of differences between actual and ring-free values of critical conversion against $1/c_0$. Systems with poly(ε-caprolactone) diol (○), poly(ε-caprolactone) triol 900 (△), and with star (✳).

**Figure 5.** Log-log plot of differences between full ($\alpha_{\mathrm{c,t}} = 1$) and actual ($\alpha_{\mathrm{c,t}}$) conversion against the difference between the actual concentration of functional groups, $c_0$, and the limiting value, $c_{0,\mathrm{lim}}$. Symbols as in Fig. 4.

$$1 - \alpha_{\mathrm{c,t}} \propto (c_0 - c_{0,\mathrm{lim}})^{\lambda} \tag{8}$$

gives for the exponent $\lambda$ the value about 0.3. The approach of $\alpha_{\mathrm{c,t}}$ to $c_{0,\mathrm{lim}}$ is thus curved upward (cf. also Fig. 2) which means that trend of stronger obstruction for formation of intermolecular bonds continues.

In modeling of the cyclization reactions (cf., e.g., Refs. [21-25]), the effect of formed rings on inter- , and intramolecular reactions was not considered so far, but it seems to be important especially for systems with diluent.

### *Equilibrium moduli*

So far, the measurements were performed only with PCL triol 900 and PCL diol 1250 systems. All measurements were performed in swollen state to eliminate possible crystallization of PCL sequences which was sometimes observed in bulk systems at room temperatures. With increasing dilution, the equilibrium moduli decrease rapidly. The values of the reduced modulus

$$G_{\mathrm{r}} \equiv \frac{G_{\mathrm{sw}}}{\mathrm{R}TA_{\mathrm{f}}(\varphi_2^0)^{2/3}\varphi_2^{1/3}} \tag{9}$$

which should be equal to the concentration of elastically active network chains (EANC) according to the theory of elasticity of Gaussian networks, plotted against $\varphi_0$ are shown in Figure 6.

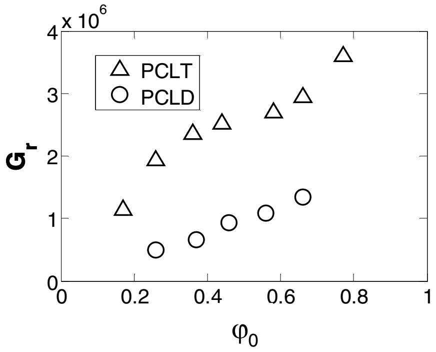


**Figure 6.** Dependence of the reduced shear modulus on the volume fraction of network components during network formation. Measurement done for networks of PCL triol 900 and networks of PCL diol 1250.

In this equation, the effect of diluent on network chain dimensions is already taken into account. The decrease in $G_r$ is associated with decrease in the number of EANC's and decrease in the concentration of possibly existing trapped entanglements. This classical interpretation is based on the assumption that network formed in the presence of diluent continues to be close to Gaussian networks - an assumption which has been more or less successfully applied to many rubbery networks [27]. However, the networks formed at higher dilutions and possibly of higher crosslink density seem to be much farther from the conditions imposed by Gaussian behavior. Close to $\varphi_{0,\mathrm{lim}}$, they are possibly more inhomogeneous than are classical networks and may remind networks of microgel-like type formed by free-radical mechanisms from polyvinyl monomers early after the system has reached the macroscopic gel point [2, 14].

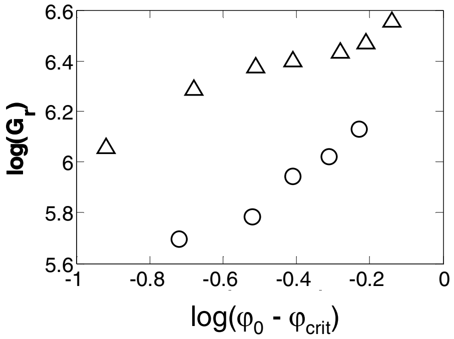


**Figure 7.** Log-log plot of reduced modulus, $G_r$ against the difference $\varphi_0$ - $\varphi_{0,\mathrm{lim}}$. Networks with PCL triol 900 (△) and with PCL diol 1250 (○).

The scaling of reduced modulus against the distance from the gel point characterized by $c_{0,\mathrm{lim}}$ is shown in Fig. 7.

$$G_\mathrm{r} \propto (\varphi_0 - \varphi_{0,\mathrm{lim}})^{\varepsilon} \qquad \mathbf{(10)}$$

It gives the exponent $\varepsilon \approx 0.65$ for PCL triol networks and less reliable plots for PCL diol networks. The theoretical scaling for $G_\mathrm{r}$

$$G_\mathrm{r} \propto (\alpha_t - \alpha_{t,c})^{t} \qquad \mathbf{(11)}$$

offers the value of exponent $t = 3$ for classical mean-field theory and $t = 2.7$ for percolation [28]. The experimental exponent for the dependence 1 - $\alpha_{\mathrm{t,c}}$ vs. $\varphi_0$ - $\varphi_{0,\mathrm{lim}}$, (relation (XX)) is $\lambda \approx 0.3$. This means that for the near-limiting –dilution networks t is about 2, considerably less than the values for the mean field and percolation models, but almost the same as found for chain crosslinking copolymerization [29, 30]. Such a difference can be explained by the differences in the structure of the classical gels and "blob-like" critical gels formed near the critical dilution limit (see sketch in Fig. 8).

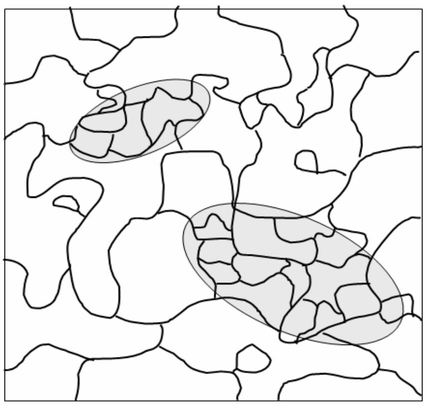


**Figure 8.** Sketch of a "blob-like" network formed in the near-to-limiting-dilution system; more internally crosslinked regions are highlighted.

## Conclusions

Measurements of gel points and equilibrium shear moduli of polyester-based polyurethane networks at different dilutions in combination with examination of scaling dependences lead to the conclusion that progressing cyclization affects the structure and behavior of the networks. The proportionality of the fraction of bonds wasted in cycles to the reciprocal concentration of functional groups is strictly valid only in the limit of tree-like structure (gel point conversion extrapolated to "infinite" concentration). The system is characterized by limiting dilution above which the gel is not formed at all even at full conversion of functional groups. These limiting dilution values vary for the system in the range 6-8 %-wt. solids (92-94 %-wt. diluent). The dependence of the equilibrium moduli on dilution points to a different structure of gels prepared near the limiting dilution of the system. It is concluded that not only the cyclization rate but also the intermolecular crosslinking rate is affected by formation of cycles.

*Acknowledgements.* DuPont Young Research Award 2004 and 2005 (MD), and European Network of Excellence "Nanostructred Multifunctional Polymer-Based Materials and Nanocomposites NANOFUN-POLY".

## References

1. Dušek K, Prins W (1969) Adv Polym Sci 6:1
2. Stepto RFT (Ed) (1998) Polymer Networks, Principles of their Formation, Structure and Properties. Blackie Academic & Professional, Thomson Science, London, New York, Philadelphia, Weinheim, pp 1-92
3. Dušek K, Dušková-Smrčková M (2000) Progr Polym Sci 25:1215
4. Dušek K (1967) J Polym Sci Pt C 16:1289
5. Dušková-Smrčková M, Dušek K (2003) Macromol Symp 198:259
6. Pascault J-P, Sautereau H, Verdu J, Williams RJJ (2002) M Dekker, New York, Basel
7. Dušek K, Patterson D (1968) J Polym Sci A-2 6:1209
8. Responsive Gels. Volume Phase Transition, Springer, Berlin, Heidelberg, New York, Dušek K (Ed) (1993) Adv Polym Sci, Vols, 109, 110
9. Dušek K, Gordon M, Ross-Murphy SB (1978) Macromolecules 11:236
10. Ilavský M, Dušek K (1986) Macromolecules 19:2139
11. Suematsu K (2002) Adv Polym Sci 156:137
12. Dušek K, Ilavský M, (1983) J Polym Sci Polym Phys 21:1323
13. Ilavský M, Bogdanova L, Dušek K (1984) J Polym Sci, Polym Phys Ed 22:265
14. Dušek K. (1982) Network Formation by Chain Crosslinking (Co)Polymerization in Development in Polymerisation 3, Haward RN (ed), Applied Science Publ, Barking, pp143-206
15. Dusek K., Galina H, Mikes J (1980) Polym Bull 3:19
16. Lewin LA, Douglas CB, Dušek K, Dušková-Smrčková M, Vlasák P (2005) Europ Coatings 81:21
17. Vlasák P, Dušková-Smrčková M, Simonsick, WJ Jr., Dušek K (2003). Polymer for Advanced Technologies (2003), Ft. Lauderdale, Abstract Book Pg. 219
18. Weissmüller M, Burchard W (1997) Polymer Int 44:380
19. Trappe V, Bauer J, Weissmüller M, Burchard W (1997) Macromolecules 30:2365
20. Šomvársky J, Dušek K, Smrčková M (1998) Comput Theor Polym Sci 8:201
21. Gordon M, Temple WB (1972) Makromol Chem 152:277
22. Dušek K, Vojta V (1977) Brit Polym J 9:164
23. Stepto RFT, Cail JI, Taylor DJR, Ward IM, Jones RA (2003) Macromol Symp 195:1
24. Cail JI, Stepto RFT, Taylor DJR (2001) Macromol Symp 171:19
25. Lang M, Goeritz D, Kreitmeier S (2005) Macromolecules 38:2515
26. Sarmoria C, Valles EM, Miller DR (1986) Makromol Chem, Macromol Symp 2:69
27. Erman B, Mark JE (1997) Structure and Properties of Rubberlike Networks. Oxford University Press, Oxford, New York
28. Adam M, Lairez D (1996) Sol-Gel Transition, in Physical Properties of Polymeric Gels. Cohen-Addad JP (ed), J Wiley & Sons, Chichester, pp 87-142
29. Adam M, (1981) Pure Appl Chem 53:1489
30. Gautier-Manuel M, Guyon E (1980) J Phys (Paris) 41:503