Diluent Induced Cyclization and Phase Separation in Polymer Networks

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Summary: The effect of the presence of diluent during network formation on the gel-point conversion, α_{crit}, and on the equilibrium elastic modulus was studied using polyurethane networks from star-shaped polyols and a star-shaped triisocyanate. The dependence of α_{crit} on reciprocal concentration of functional groups, $1/c_o$, extrapolated well for $1/c_o \rightarrow 0$ to the value calculated corresponding to the ring-free system. The decrease of the equilibrium modulus and the concentration of elastically active network chains (EANC) in dependence on the volume fraction of polymerizable compounds (solids) ϕ_2^0 was curved downwards and extrapolated to the limiting dilution of the system at which no gel was formed when the conversion of functional groups was 100%. Some samples exhibited phase separation in the form of macro-syneresis which affected ϕ_2^0. The continuous change of gel volume as a result of phase separation was obtained by solving an integral equation respecting the thermodynamic stability of the system. The change of the concentration of EANCs obtained from equilibrium modulus was translated into the intermolecular conversion calculated using the branching theory. The intermolecular conversion depended linearly on the shift of the gel-point conversion.

Keywords: cyclization; elasticity; gelation; phase separation; polymer network

Introduction

Polymer networks are often prepared in the presence of non-polymerizable diluents. Diluents are present during formation of binders designed for protective coatings or when majority of hydrogels are prepared. Diluents are also applied in preparation porous polymeric materials, mainly inducing the phase separation.[1–6] The presence of diluents enhances the intramolecular cross-linking at the expense of intermolecular bond formation, weakens interchain interactions. It also may induce formation of static fluctuations in segment densities, and can give rise to one of the forms of phase separation.[1,3–5,7]

Cyclization (ring-closing, intramolecular cross-linking) occurs by formation of a bond between functional groups already connected by a sequence of bonds. Cyclization before the gel point is defined unambiguously: by its formation, the number of molecules in the system remains the same - the molecular weight does not increase. By formation of an intermolecular bond, the number of molecules decreases by one (Figure 1a).

The gel existing beyond the gel point contains many cyclic structures which are formed by reaction between the groups in the gel. By gel-gel reactions, the cycle rank of the gel increases. Such closed circuits are composed mainly of elastically active network chains (EANCs) contributing to equilibrium elasticity. However, some of

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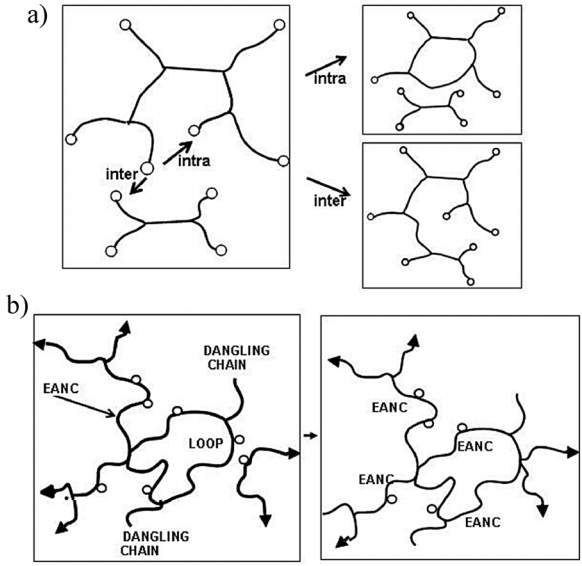


Figure 1.
Inter- and intramolecular cross linking before the gel point (a) and activation of an elastically inactive loop (b); ○ functional group, ➔ continuation to infinite structure.

them (loops) are elastically inactive and do not contribute to equilibrium elasticity and chains in some of other cyclic structures contribute only partially. As the cross-linking reaction proceeds, some of the elastically inactive loops are transferred into states in which the chains acquire elastic activity[1] (Figure 1b).

The extent of cyclization depends on the functionality of the precursors and topological distances between functional groups and flexibility of connecting paths. It increases with decreasing group concentration and can be dependent on intra- and intermolecular excluded volume. The excluded volume effects come into play in systems with strongly interacting solvent and in more dilute systems. Cyclization is dependent on the mechanism of the cross-linking reaction. Cyclization is as a rule stronger for initiated chain reactions than for step growth polymerizations.[1,8–15]

In this contribution, we have concentrated on the effect of the amount of the diluent on the shift of gel point conversion and on lowering of the equilibrium modulus of elasticity for several polyurethane networks obtained by endlinking of star-shaped precursors. It was found[16–19] that hydrogels prepared from star-shaped precursors did not show up any inhomogeneities. The studies of the effect of dilution have revealed several cases of cross-linking induced phase separation in the form of macrosyneresis which yields homogeneous gels of smaller volume than was the initial one with separated diluent as bulk phase. This type of phase separation is classified as *macro*syneresis in contrast to formation of dispersed phases by *micro*syneresis (Figure 2). For the determination of the concentration of EANCs from elasticity or swelling experiments, this change in volume and the resulting chain conformation has to be taken into account. The interrelations[20] between pregel cyclization and lowering of the modulus of elasticity of gels are briefly discussed.

Experimental Part

Chemicals

The diluents, solvents, and other chemicals were of reagent or analytical grade supplied by Sigma-Aldrich and used as received. If necessary, water was removed by molecular

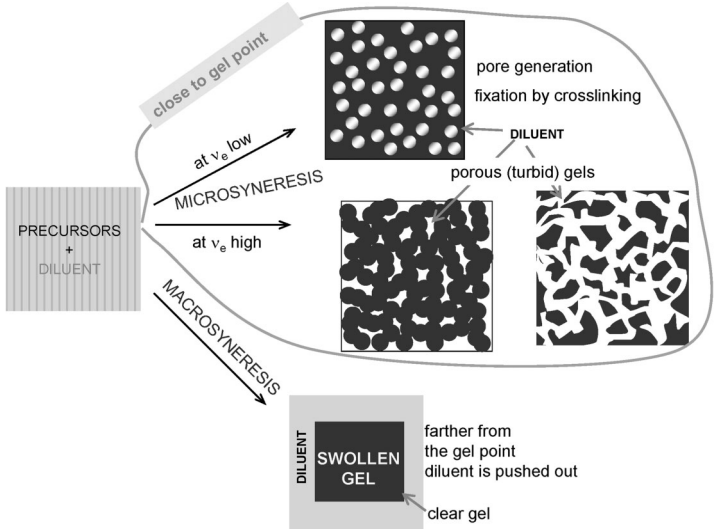


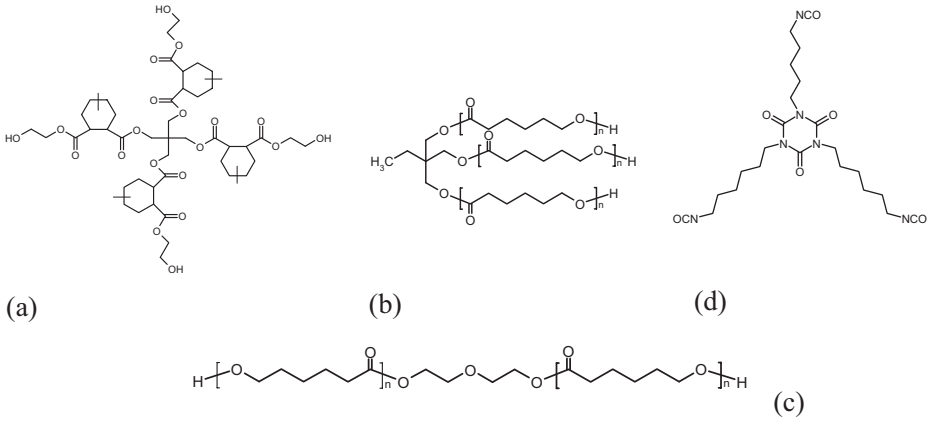
Figure 2.
Forms of phase separation in the presence of a diluent during cross-linking.

sieves, so that its content did not exceed 0.01 wt.-%. As isocyanate components, trimers of 1,6-diisocyanatohexane, Desmodur N3300 and Desmodur N3600 kindly provided by Bayer Co. were used.

Precursors of Networks

The tetrafunctional star (4-f STAR, Figure 1a), was an oligoester with primary OH groups located at the arm ends and was prepared by reaction of a pentaerythritol with (substituted) hexahydrophthalic anhydride and subsequently functionalized with ethylene oxide. Its number-average molecular weight was 942 g/mol and its number-average functionality determined from mass spectroscopy was $\langle f_A \rangle_1 = 3.96 \approx 4.0$.

Polycaprolactone triols (PCLT 300, PCLT 900) and polycaprolactone diol (PCLD 1250) were purchased from Sigma-Aldrich. Their molecular weights were approximately 300, 900 and 1250 g/mole (Scheme 1). The values of the number-average functionality $\langle f_A \rangle_1$ for this particu-



Scheme 1.
Structure of precursors. (a) 4-f STAR, (b) polycaprolactone triols,(c) polycaprolactone diol, (d) trimer of 1,6-diisocyanatohexane.

lar set of samples of PCLD1250, PCLT900, PCLT300, and 4-f STAR, were equal, respectively to 1.87, 2.95, 2.87, and 3.98. The second-moment functionality average $\langle f_A \rangle_2 = 1.93, 2.97, 2.93$, and 4.0, respectively. ($\langle f_X \rangle_1 = \sum_{f_X} f_X n_f, \langle f_X \rangle_2 = \sum_{f_X} f_X^2 n_f / \sum_{f_X} f_X n_f$ where n_f is the number fraction of molecules having f_X functional groups X.

The isocyanate component was a star–shaped cyclotrimer of 1,6-diisocyanatohexane which contained higher oligomers and possibly a certain quantity of molecules containing urea and biuret groups. Desmodur N3600 was purer than Desmodur N3300. The composition of the commercial samples varied somewhat from lot. The determination of average functionality by ESI and MALDI TOF FT MS has been described in ref. [20]

Preparation of Networks

Hydroxy-functional precursors were dissolved in suitable solvents to get 20–80 wt.-% solutions. Dibutyltin dilaurate (500 ppm based on solids) as catalyst and Desmodur N3300 or N3600 were added. The solution was poured into a glass mold to make sheets (about 2 mm thick) and left to react to achieve full conversion of NCO groups. The decrease of the concentration of NCO groups was determined by FTIR spectroscopy (band at 2273 cm^{-1} related to the intensity of the reference C–H stretching band at 2930 cm^{-1}).

Determination of Critical Conversion

The critical time and critical conversion were determined by checking for full solubility of the system after adding a solution of di-n-butylamine in THF. This method was combined by determination of gel fraction w_g and extrapolation their dependence ion conversion to $w_g = 0$. The conversions of NCO groups were determined by FTIR spectroscopy in parallel.

Characterization of Networks

Swelling

The volume fraction of polymer in the swollen sample (ϕ_2) was calculated from weights of the swollen (m_{sw}) sample and dry sample after extraction (m_d) and specific gravities of the polymer (ρ_p) and solvent (ρ_s), $\phi_2 = [m_{pol}/\rho_{pol}] / [m_{pol}/\rho_{pol} + (m_{sw} - m_{pol})/\rho_{solv}]$. The volume fraction of polymerizable material during network formation called "solids" is given by

$$\phi_2^0 = [m_{pol}/\rho_{pol}] / [m_{pol}/\rho_{pol} + m_{solv}/\rho_{solv}].$$

Equilibrium Modulus

Dynamic mechanical measurements (DMA) were performed using a Dynamic mechanical analyser Tritec 2000 (Triton Technology Ltd.). Samples were measured in the equilibrium swollen state. In the swollen state, the frequency dependence of the complex Young modulus $E^* = E' + iE''$ (E′ is storage and E″ loss modulus) was measured at ambient temperature in the frequency range from 0.1 Hz to 30 Hz. Experimental details are available in ref. [20]

Results and Discussion

Critical Gel-Point Conversion

The gel-point conversion of NCO groups $(\alpha_{NCO})_{crit} \equiv \alpha_{crit}$ for stoichiometric systems has been determined as a function of dilution characterized by the initial concentration of all reactive groups c_0 (mol/cm^3) or volume fraction of polymerizable components ϕ_2^0; the fraction of diluent being $\phi_1^0 = 1 - \phi_2^0$; and $\phi_2^0 = c_0/(c_0)_{bulk}$. Since the extent of cyclization decreases with increasing concentration, the extrapolation of α_{crit} to the hypothetical $(1/c_0) \to 0$ or $1/\phi_2^0 \to 0$ should eliminate the effect of cyclization and give the critical conversion for the ring-free case. This quantity can be calculated from the branching theory that assumes that all bonds are intermolecular. For equal reactivity of hydroxyl (A) and isocyanate (B) groups, respectively, the value of α_{crit} is given by the Stockmayer equation

$$\alpha_{crit}^2 = \left[(f_A - 1)(\langle f_B \rangle_2 - 1)\right]^{-1} \quad (1)$$

An analysis of the dependence of α_{crit} on $1/\phi_2^0$ under certain simplifying assumptions

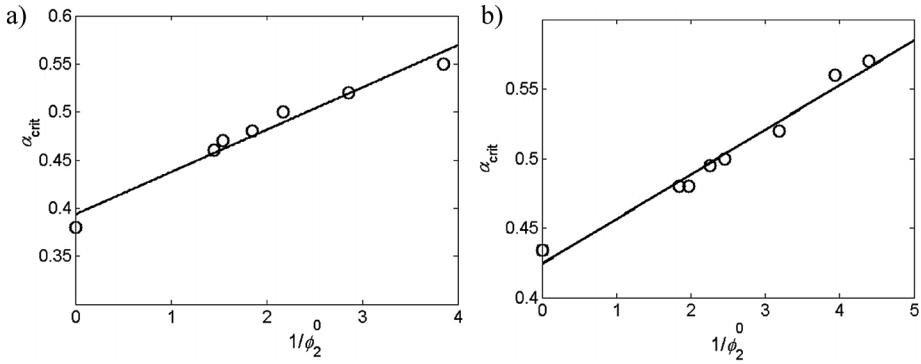


Figure 3.
(a) Gel-point conversion, α_{crit},4-f STAR with Desmodur N3300; diluent – methyl amyl ketone. (b) Gel-point conversion, α_{crit}, PCLT-900 with Desmodur N3300; diluents – methyl amyl ketone and diglyme.

shows that this dependence should be linear. This has been confirmed experimentally in most cases.[3] The dependence of the critical conversion on dilution for two of the precursors is shown in Figure 3.

Although some of the plots show up signs of curvature, the deviations from linearity are within experimental error. The intensity of cyclization is characterized by the slope of the dependences. It depends mainly on precursor functionality and size of the smallest cycle (arm length).

Within experimental error, no difference was found when diglyme and methyl amyl ketone (somewhat poorer solvent) were used as diluents. Up to the gel point, the reaction products were well soluble in the both diluents.

Figure 4 shows the fraction of bonds lost in closing of cycles for cross-linking in systems containing 40 wt.-% diluent which is a typical value for solvent-based high-solids coatings.

The binder called ACRYLCO-1 was a copolymer of vinyl monomers with 2-hydroxyethyl methacrylate (HEMA) of $\langle f_A \rangle_2 \approx 14$; ACRYLCO-GRL and ACRYLCO- GRB with linear and branched side chains, respectively, were similar copolymers but of higher molecular weight containing also secondary OH groups and chain extended (internally diluted) of $\langle f_A \rangle_2 \approx 10$, and the hyperbranched was based on 2,2-dimethylolpropionic acid of $\langle f_A \rangle_2 \approx 16$.

Swelling and Phase Separation

The equilibrium swelling degree increases with increasing dilution. Some samples of the highest dilutions take up in equilibrium less diluent than was added before network formation (Figure 5). This indicates phase separation during network formation – expulsion of a part of solvent out of the sample at higher conversions. The gel contracts and remains transparent. The memory factor ϕ_2^0 changes which should be respected in calculating the concentration of EANCs from equilibrium modulus.

The phase separation can start before, at or after the gel point. After the gel point, phase separation can happen when the crosslink density and possibly the associated changes of polymer segment–solvent interactions are such that the gel cannot absorb the amount of the diluent initially added. The key role is played by the memory term, ϕ_2^0. Before phase separation,

Table 1.
Slopes of α_{cirt} *vs.* $(1/\phi_2^0)$

precursor	4f-STAR	PCLT300	PCLT900	PCLD1250
slope α_{cirt} *vs.* $(1/\phi_2^0) \times 10^2$	4.25	4.00	2.80	2.50

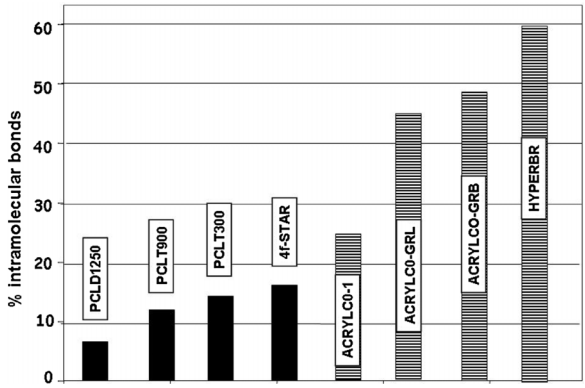


Figure 4.
Fraction of intramolecular bonds of all bonds formed at the gel point for different precursors prepared in the presence of 40 wt.-% diluent (60 wt.-% solids). Some previously obtained results on higher-functional polyols; statistical OH-functional precursors and hyperbranched polymers[21] are added.

the activity of the solvent a_1 is less than one (the vapor pressure p_1 is lower than the vapor pressure over pure solvent). As cross-linking proceeds, the solvent activity increases while the gel volume remains constant. At the point of phase separation if sol fraction is negligible, $\phi_2 = \phi_2^0$, while $a_1 = 1$ (cf., ref. [22]). Beyond this point, $a_1 = 1$ continues to hold but the gel volume (its degree of swelling) decreases (Figure 6).

Assuming that the reaction is slow enough, so that the swelling equilibrium can be established, the conditions, $\phi_2 = \phi_2^0$, $a_1 = 1$ give for a Gaussian affine or phantom network the same relation

$$\ln(1-\phi_2^0) + \phi_2^0 + \chi(\alpha_{cs})(\phi_2^0)^2 + V_{m1}\phi_2^0\nu_e(\alpha_{cs})\left(\frac{f_e-2}{f_e}\right) = 0 \qquad (2)$$

where χ is the Flory-Huggins (concentration dependent) polymer-solvent interaction parameter, V_{1m} is the molar volume of the diluent, f_e is the average number of EANCs issuing from an ekastically active junction[23], and α_{cs} is the critical value of conversion of functional groups in the moment of phase separation. At this state ($\phi_2 = \phi_2^0$), the network chains are in their state of ease, and the last term of Equation (2) merely reflects the entropy loss when cross-links exist within the gel and the cycle rank characterized by ν_e is building up. By this term, the mixing of cross-linked gel with solvent differs at this state of approximation from mixing of a collection of infinite (branched) molecules with solvent. - By increasing the conversion, the diluent continues separating: a_1 remains equal to 1, but the memory term ϕ_2^0 starts changing because the new EANCs are formed at their state of ease corresponding to a volume smaller than that before phase separation. In the final dry network, the EANCs are thus less compressed. Beyond

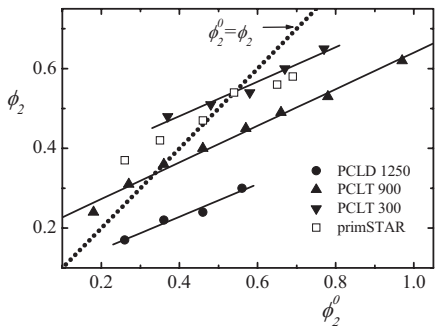


Figure 5.
Equilibrium degree of swelling of networks in diglyme at 25 °C, expressed as volume fraction of polymer, ϕ_2, in dependence on dilution with diglyme during network formation, expressed as volume fraction of solids, ϕ_2^0.

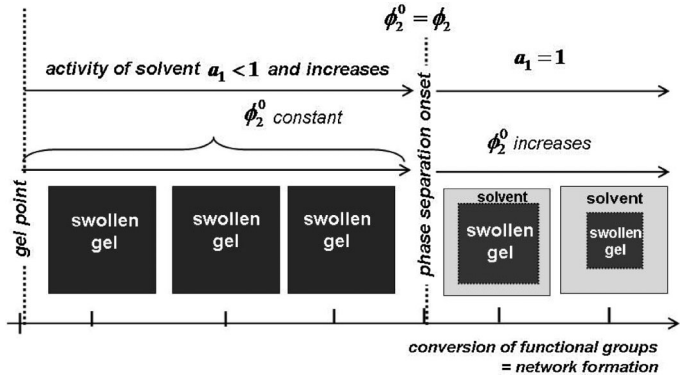


Figure 6.
Cross-linking of a system with diluent undergoing phase separation after the gel point.

the point of phase separation, the condition for swelling equilibrium with the diluent reads

$$\ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 + V_{m1}\nu_e[A\phi_2^{1/3}(\phi_{2sep}^0)^{2/3} - B\phi_2] = 0 \quad (3)$$

Where ϕ_2^0 is replaced by ϕ_{2sep}^0. A and B are the factors which, in the Flory–Erman junction–fluctuation theory,[4] assume the limiting values $A = (f_e - 2)/f_e$ and $B = 0$ for phantom network and $A = 1$ and $B = 2/f_e$ for affine network. The quantities ϕ_2, χ, ν_e, and ϕ_{2sep}^0 depend on conversion α. For conversions at $\alpha > \alpha_{cs}$, the memory term ϕ_{2sep}^0 is determined by the equation

$$\phi_{2sep}^0\,\nu_e(\alpha) = (\nu_e)_{cs}\,\phi_2^0 + \int_{(\nu_e)_{cs}}^{\nu_e(\alpha)} \phi_2(\alpha)d\nu_e = \int_{\alpha_{cs}}^{\alpha} \phi_2(\alpha)\frac{d\nu_e(\alpha)}{d\alpha}d\alpha \quad (4)$$

The values of ϕ_{2sep}^0 are then used for calculation of ν_e from the equilibrium modulus. The ϕ_{2sep}^0 values are obtained by solving the integral Equation (4) in conjunction with Equation (3) numerically. The interaction parameter depends on concentration and thus also on conversion. This dependence was obtained from the equilibrium swelling degree and equilibrium modulus of samples prepared at different dilutions where phase separation did not occur. We have calculated $\phi_{2sep}^0\nu_e(\alpha)$ by choosing increments of $\delta\alpha$ (10^{-4} or 10^{-5}) and found the corresponding $\delta\nu_e$ from the ν_e - α dependence for samples where phase separation did not occur. Finding a new value of ϕ_2, the increment $\phi_2\delta\nu_e$ was calculated.

Equilibrium Modulus and Concentration of Elastically Active Network Chains (EANCs)

The storage modulus, E', of swollen samples was independent of frequency in the range 0.01–10 Hz. The modulus falls to zero at the limiting value of dilution for which the gel point is shifted to full conversion of functional groups[15] and beyond which a coherent gel does not exist. According to the theory of Gaussian networks, the tensile stress is related to macroscopic deformation ratio relative to the isotropic swollen state, Λ, as

$$\sigma_{sw} = f/S_{sw} = RTA\nu_e\phi_2^{1/3}(\phi_2^0)^{2/3}(\Lambda - \Lambda^{-2}) = 3RTA\nu_e\phi_2^{1/3}(\phi_2^0)^{2/3}\varepsilon + \ldots. \quad (5)$$

where f is the tensile force, S_{sw} the cross-section area of swollen sample, and $\varepsilon = \Lambda - 1$. Other quantities have been defined above. For samples that underwent

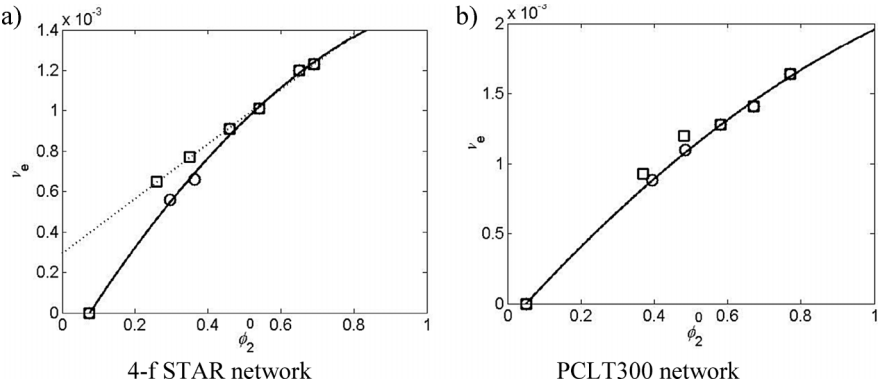


Figure 7.
Concentration of EANCs as a function of volume fraction of solids, ϕ_2^0: squares - ϕ_2^0 constant, not considering phase separation; circles - effect of phase separation respected, $\phi_{2\,sep}^0$ used; full lines: interpolation.

phase-separation during their preparation, ϕ_2^0 should be replaced by ϕ_{2sep}^0 (cf., Equation (3), (4)). Thus, the small-strain Young modulus E is given by the equation

$$E \cong E' = 3RTA\nu_e\phi_2^{1/3}(\phi_{2sep}^0)^{2/3} \qquad (6)$$

The examples of dependence of ν_e on ϕ_2^0 for samples that phase-separated is shown in Figure 7a,b.

For the samples where phase separation took place and ϕ_2^0 was replaced by ϕ_{2sep}^0 and by the result of this replacement also the values of ν_e were somewhat different. The largest difference was found for the network of 4f-STAR. After correction, the dependence smoothly proceeds to the limiting dilution limit at which coherent gels cease to be formed.

Scaling of equilibrium modulus and degree of swelling against ϕ_2^0 has been a subject of numerous papers.[24–26] For the four series of samples discussed here, the average values of exponents of the scaling relations

$$E' \propto (\phi_2^0)^x \qquad \phi_2 \propto (\phi_2^0)^y \qquad (7)$$

were equal to $x = 1.77$ and $y = 0.54$.

The results were compared with those found earlier[26] for PDMS networks diluted by non-functional PDMS; x varied with lengths of EANCs from $x = 2.07$ for EANCs of $M_n = 10^5$ to $x = 1.52$ for EANCs of $M_n = 10^4$. In our systems of relatively high cross-link density, entanglements did not play any important role and the value of x was closer to that of low M_n limit; the exponent y decreased from 0.65 to 0.50. Our dependences did not fit the limiting dilution data ($E = 0$ for $\phi_2^0 = \phi_{2lim}^0$) because of different macrogelation mechanism (microgel formation first followed by ''chemical coagulation'').[1,8,11] Using Equation (6) valid for near to theta-state and experimental values of exponents $x = 1.77$ and $y = 0.54$, the concentration of EANCs, ν_e, scales with ϕ_2^0 as $\nu_e \propto (\phi_2^0)^z$ with $z = 0.92$ which is in absolute value close to the scaling factor -1 in $(\phi_2^0)^{-1}$ satisfying the shift of the gel point conversion. Earlier predicted value for the exponent was $z = 4/3$ for Θ-solvents[27] and it was based on disentanglement by dilution, a case which does not apply here.

Interrelation between Pregel Cyclization and Lowering of the Modulus

It is interesting to examine whether pregel cyclization can be correlated with the decrease of modulus by dilution. The effective crosslink density (i. e., that without contribution from chains in elastically inactive loops) can be translated into the intermolecular conversion, α_{inter}, corresponding to experimental ν_e (calculated from equilibrium modulus) at conversion of

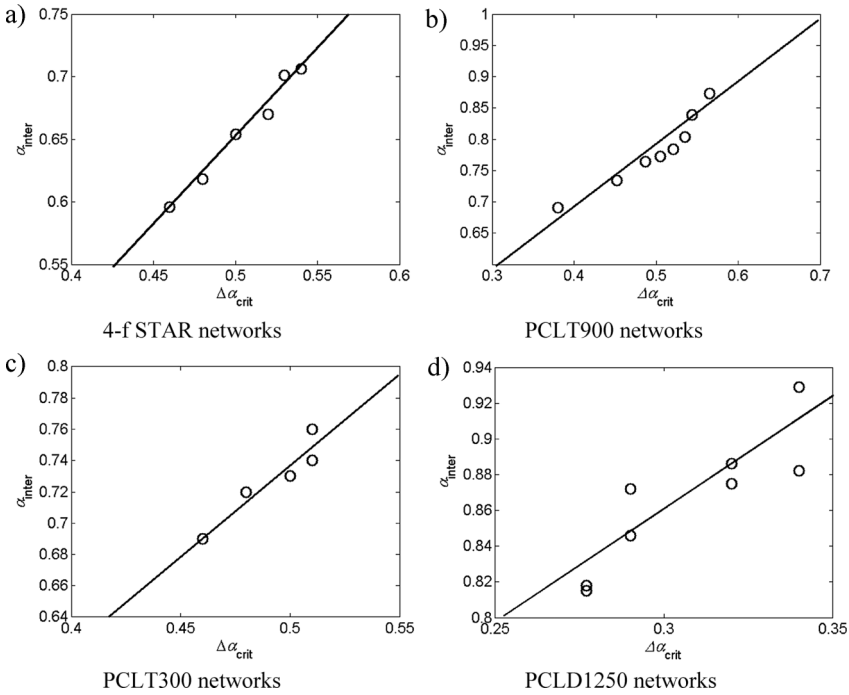


Figure 8.
Dependence of intermolecular conversion of functional groups on $\Delta\alpha_{crit} = 1 - \alpha_{crit}$.

functional groups 100%. These values of α_{inter} were calculated using the theoretical dependence of ν_e on α_{inter} derived by the branching theory[20]. The following results were obtained (Figure 8).

The difference $\Delta\alpha_{crit} = 1$ - α_{crit}, where α_{crit} is the experimentally determined critical gel-point conversion. For $\alpha_{crit} = 1$, $\nu_e = 0$ at limiting dilution. Also, $\nu_e = 0$ at the gel point, when $\alpha_{inter} = (\alpha_{crit})_{rf}$; $(\alpha_{crit})_{rf}$ is the ring-free value of gel-point conversion calculated from the branching theory and obtained by extrapolation of experimental α_{crit} to $1/\phi_2^0 \rightarrow 0$. One can see that a linear correlation of the shift of the gel point and lowering of modulus exists. This means that there exists a correlation between pregel cyclization and lowering of effective cross-link density caused by dilution. In ref.[20], a method has been proposed to predict the effect of dilution on the concentration of EANCs in a series of samples of different dilutions. Experimentally determined critical gel-point conversion and equilibrium modulus of a sample prepared at one value of ϕ_2^0 and the theoretical values calculated for the ring-free case.

Conclusion

For a series of polyurethane networks from star-shaped precursor, with increasing dilution the gel point was shifted to higher conversions of functional groups and the equilibrium modulus decreases with increasing dilution. The percentage of bonds wasted in cycles at the gel point increased with increasing functionality of the precursors and with their decreasing molecular mass. Some of the samples containing more diluent showed up phase separation in the form of macrosyneresis. For such samples, the memory term ϕ_2^0 was larger than its initial value because the newly formed elastically active network chains were formed in a gel volume smaller than the initial one. The correct value

resulted from solution of an integral equation. This value was used for calculation of the concentration of EANCs. A correlation was found between the shifts of the gel point and lowering of the concentration of EANCs resulting from dilution during network formation.

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