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# Solvent Activity Changes and Phase Separation During Crosslinking of Coating Films

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**Summary:** Changes in solvent activity and thermodynamic stability of a system undergoing crosslinking in the presence of a solvent are modeled by combination of branching theory with thermodynamics of polymer solutions and swelling of a crosslinked polymer. The system is considered as a quasiternary one in which the solvent, polydisperse soluble polymer (sol) and crosslinked network, respectively, represent the components. Crosslinking brings about growth of polymer structures but also changes in polymer-solvent interactions. The results are compared with onset of phase separation and changes in evaporation rates from films formed from a hydroxy-functional star oligomer and triisocyanate.

**Keywords:** crosslinking, phase separation, polymer-solvent interaction, solvent activity, swelling

## Introduction

Solvent-based coating films are formed by simultaneous crosslinking of polymer network precursors and solvent evaporation. Usually, two-component systems are used: oligomeric or polymeric component carrying functional groups and a crosslinker of lower functionality (2-4) and lower molecular weight. Film formation by simultaneous crosslinking and solvent evaporation is a complex process in which the crosslinking rate and network structure development depend on the content and nature of the solvent and solvent evaporation depends not only on solvent volatility but also on the structure of the crosslinking system. Moreover, in some systems these changes induce a transition of the system from rubbery into glassy state and all important processes become controlled by segmental mobility.[1,2] In a drying film, diffusion is driven by gradients of chemical potentials. Evaporation of the solvent is controlled by solvent vapor pressure and this is determined by the solvent activity in the film. The solvent activity decreases with decreasing solvent concentration and usually increases with advancing reaction because the molecular weight of polymeric components or their crosslink density increase. Sometimes, the system becomes thermodynamically

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unstable and phase separation sets in. In a crosslinked system, this happens when the content of solvent is equal or exceeds the maximum (equilibrium) degree of swelling of the network.[3-5] This is general case of reaction-induced phase separation widely studied.[6]

In this contribution, the changes of solvent activity and possible onset of phase separation resulting from crosslinking reaction in the presence of various amounts of solvent is studied theoretically and compared with some experimental data obtained for crosslinking system of a hydroxy-functional oligomer (tetrafunctional star) crosslinked with a triisocyanate. Before the gel point, the crosslinking system is considered as pseudobinary and, beyond the gel point, as pseudoternary; solvent, polydisperse branched polymer (sol), and crosslinked gel being considered as components. For modeling of the changes, the network formation theory is combined with the theory of polymer solutions/swelling of crosslinked gels. In this first approximation, the interactions are described by simple Flory-Huggins approach with concentration independent interaction parameters and the build-up of crosslinked structures using the statistical theory of branching processes in its ring-free version.

## Experimental

The hydroxy-functional precursor was a star-shaped polyester with 4 primary hydroxyls of hydroxyl number 235.2 mg KOH/g and molecular weight 1031 g/mol was prepared by hyroxyl-anhydride-acid-epoxide reaction[7]. The polyisocyanate used was Desmodur 3300 (Bayer) - a trimer of 1,6-diisocyanatohexane of molecular weight 690 g/mol (VPO), number-average functionality 3.5 and second-moment average functionality 3.65.

The progress of reaction was monitored by transmission FTIR using the absorption by NCO groups at 2270 cm$^{-1}$ or by chemical method in which unreacted isocyanate groups are reacted with excess of n-dibutylamine and the unreacted amine titrated by hydrochloric acid. Also, attenuated total reflection (ATR) mode of FTIR was used for monitoring NCO group conversion in the surface layer.

Evaporating films were cast on a metallic substrate using an blade applicator. Their typical wet thickness was 200 μm. Solvent evaporation was monitored by an automatic balance placed in an environmental chamber. Non-evaporating films, where the solvent concentration remained constant during crosslinking, were prepared between two glass plates. All experiments were carried out at temperature 25±2°C.

Phase separation occurred in the form of macrosyneresis beyond the gel point and was observed visually as liquid separated out of the gel or by ATR FTIR when the signals assigned to the polymer suddenly disappeared. The volume of the separated liquid was not determined.

## Theoretical

**Thermodynamics of Mixing and Swelling:** The solvent vapor pressure, $p_1$, is proportional $p_1^0$ to the vapor pressure of the pure solvent and its activity in the film, $a_1$

$$p_1 = p_1^0 a_1 = p_1^0 c_1 \gamma_1 \tag{1}$$

where $\gamma_1$ is the activity coefficient and $c_1$ is the solvent concentration. The solvent activity is dependent on (a) solvent concentration, (b) thermodynamic interactions between segments of component units, and (c) structure of the polymer: molecular weights of sol, sol and gel fractions, and crosslink density that are functions of conversion of reactive groups. During film formation, the solvent concentration decreases by evaporation (a negative contribution to $a_1$ and the polymer structure develops (a positive contribution to $a_1$). Moreover, the thermodynamic interactions between solvent molecules and polymer segments change because reactive groups are transformed into bonds. In adhering films, stresses in plane develop. The resulting anisotropy of the swollen film was shown to have an effect on solvent activity[8]; this effect, however, will not be considered here.

The thermodynamics of the system is described by the Flory-Huggins-Staverman (FHS) theory of polymer solutions and Flory-Erman theory of rubber elasticity.[9]-[13] A similar Gibbs energy function as formulated in Ref. 14 was used by Frisch and Binder[15] for theoretical treatment of phase separation in interpenetrating polymer networks. These systems were considered as binary weakly crosslinked non-reactive systems with no solvent and no sol fraction.

The change in the Gibbs energy, $\Delta G$, associated with mixing solvent with polymer component is assumed to be composed of mixing and network terms (beyond the gel point).

$$\Delta G = \Delta G_{\mathrm{mix}} + \Delta G_{\mathrm{net}} \tag{2}$$

The FHS mixing term for a ternary system (component 1 is solvent, component 2 soluble polymer, component 3 network polymer) is given by the equation[12],[13]

$$\frac{\Delta G_{\mathrm{mix}}}{NkT} = \frac{\phi_1}{m_1}\ln\phi_1 + \frac{\phi_2}{m_2}\ln\phi_2 + \frac{\phi_3}{m_3}\ln\varphi_3 + \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3 \tag{3}$$

where $N$ is the total number of lattice sites (occupied by polymer segments and solvent molecules), $\phi_1, \phi_2$, and $\phi_3$ are volume fractions of the respective components and $\chi_{ij}$ are (concentration independent) binary interaction parameters. The quantities $m_i$ are the ratios of volumes of component $i$ to the volume of the lattice site; often a polymer segments is considered to occupy one lattice site and $m_i = V_i/V_s$, for polymers with identical segments but different degree of polymerization, $P_i$ $m_i \propto P_i$. Sometimes the polymer segment is chosen such that $V_s = V_1$; then $m_2 = P_2 V_m$ ($V_m$ is molar volume of polymer segment) and $m_1 = 1$ and $1/m_3 = 0$, because component 3 (network has infinite degree of polymerization).

The term $\Delta G_{net}$ is associated with deformation of the elastically active network chains (EANC) and other deformation dependent entropic changes originating in fluctuation of junctions (crosslinks). For Gaussian chains

$$\frac{\Delta G_{net}}{kT} = An_e\left(\frac{L_x^2}{L_{0x}^2} + \frac{L_y^2}{L_{0y}^2} + \frac{L_z^2}{L_{0z}^2} - 3\right) - Bn_e \ln \frac{L_x L_y L_z}{L_{0x} L_{0y} L_{0z}} \qquad (4)$$

where $L_k$ is the length of the deformed sample in the direction of the $k$ axis; $L_{0k}$ is the corresponding value in reference state at which the chains are at their state of ease; $n_e$ is the number of elastically active network chains; $A$ is the front factor which, within the framework of the Flory-Erman junction-fluctuation rubber-elasticity theory, varies between $(f_e - 2)/f_e$ and 1 for phantom and affine models, respectively; $f_e$ is the average functionality of an elastically active crosslink; $B$ varies between 0 (phantom network) and $2/f_e$ (affine network).

The deformation ratios with respect to the reference state are defined by $\Lambda_k = L_k / L_{0k}$ and for an isotropic system $\Lambda_k(k=x,y,z) \equiv \Lambda$; $\Lambda$ is related to volume fraction of the network polymer $\phi_3$, and reference state at network formation, given by the volume fraction of the polymer at network formation $\phi_0$, as $\Lambda = (\phi_3)^{-1/3}(\phi_0)^{1/3}$, so that

$$\frac{\Delta G_{net}}{kT} = 3n_e\left(A\Lambda^2 - B\ln \Lambda^3\right) = 3n_e\left(A\phi_3^{-2/3}\phi_0^{2/3} - B\ln(\phi_0/\phi_3)\right) \qquad (5)$$

By passing to moles of EANC's and differentiating $\Delta G$ with respect to the number of moles of component I, the change of chemical potential, $\Delta\mu_I$ is obtained. The expression for the change of chemical potential of the solvent $\Delta\mu_1$ contains structural parameters of the crosslinked system (molecular weight averages, sol and gel fractions and their composition and concentration of EANC's) which are a function of conversion. They will be derived first.

**Structural Changes Resulting from Crosslinking:** The development of the network structure is described theoretically by the statistical Theory of Branching Processes (TBP). (cf., e.g., Refs.[16],[17]). The components A and B, are considered tetrafunctional and trifunctional, respectively. The component A carries $f_A$ groups of type A, and the component B $f_B$ groups B. All functional groups A and all functional groups B, respectively, have the same reactivity that is independent of conversion; intramolecular reactions are not considered at present. Due to limited space of this contribution, only basic results of the theoretical derivation are summarized below.

The basic probability generation function (pgf), $F_{0n}(z_A,z_B)$, for the distribution of reaction states of building units with respect to the number and type of formed bonds reads

$$F_{0n}(z_A, z_B) = n_A(1-\alpha_A+\alpha_A z_B)^{f_A} + n_B(1-\alpha_B+\alpha_B z_A)^{f_B} \tag{6}$$

where $z_A$, $z_B$ are variables of the pgf, $\alpha_A$ and $\alpha_B$ are conversions of A and B groups, and $n_A$ and $n_B$ are molar fractions of components A and B, respectively. The critical conversion at the gel point for this system is described by the well known Stockmayer equation

$$(\alpha_A\alpha_B)_{\text{crit}} = \frac{1}{(f_A-1)(f_B-1)} \tag{7}$$

The extinction probabilities for bonds B→A and A→B, $v_A$ and $v_B$, respectively, are given by

$$v_A = (1-\alpha_A+\alpha_A v_B)^{f_A-1} \qquad v_B = (1-\alpha_B+\alpha_B v_A)^{f_B-1} \tag{8}$$

The parameters needed in the thermodynamic equations are the weight or volume fractions of sol ($w_s$, $\varphi_s$) and gel ($w_g$, $\varphi_g$), number-average molecular weight or molar volume of sol ($(M_n)_s$, $(V_n)_s$), and conversions of A and B groups in sol and gel ( $(\alpha_A)_s$, $(\alpha_B)_s$, $(\alpha_A)_g$, $(\alpha_A)_g$):

$$w_s = w_A(1-\alpha_A+\alpha_A v_B)^{f_A} + w_B(1-\alpha_B+\alpha_B v_A)^{f_B} \qquad w_g = 1-w_s \tag{9}$$

$$\varphi_s = \varphi_A(1-\alpha_A+\alpha_A v_B)^{f_A} + \varphi_B(1-\alpha_B+\alpha_B v_A)^{f_B} \qquad \varphi_g = 1-\varphi_s \tag{10}$$

$$(M_s)_n = \frac{n_A M_A(1-\alpha_A+\alpha_A v_B)^{f_A} + n_B M_B(1-\alpha_B+\alpha_B v_A)^{f_B}}{n_A(1-\alpha_A+\alpha_A v_B)^{f_A} + n_B(1-\alpha_B+\alpha_B v_A)^{f_B} - n_A f_A \alpha_A v_B(1-\alpha_A+\alpha_A v_B)^{f_A-1}} \tag{11}$$

$$(V_s)_n = \frac{n_A V_A(1-\alpha_A+\alpha_A v_B)^{f_A} + n_B V_B(1-\alpha_B+\alpha_B v_A)^{f_B}}{n_A(1-\alpha_A+\alpha_A v_B)^{f_A} + n_B(1-\alpha_B+\alpha_B v_A)^{f_B} - n_A f_A \alpha_A v_B(1-\alpha_A+\alpha_A v_B)^{f_A-1}} \tag{12}$$

$$(\alpha_A)_s = \frac{\alpha_A v_B}{(1-\alpha_A+\alpha_A v_B)} \qquad (\alpha_B)_s = \frac{\alpha_B v_A}{(1-\alpha_B+\alpha_B v_A)} \tag{13}$$

$$(\alpha_A)_g = \frac{1-v_B(1-\alpha_A+\alpha_A v_B)^{f_A-1}}{1-v_B(1-\alpha_A+\alpha_A v_B)^{f_A}} \qquad (\alpha_B)_g = \frac{1-v_A(1-\alpha_B+\alpha_B v_A)^{f_B-1}}{1-v_A(1-\alpha_B+\alpha_B v_A)^{f_B}} \tag{14}$$

$w_A$ and $w_B$ are mass fractions of components A and B, $M_A$ and $M_B$ the respective molecular weights, and $V_A$ and $V_B$ molar volumes. The concentration of elastically active network chains (EANC) is derived from the number of EANC's per building unit, $N_e$,

$$\begin{aligned} N_e = {} & (n_A/2)\left[(f_A\alpha_A(1-v_B))(1-(1-\alpha_A+\alpha_A v_B)^{f_A-1}) - f_A(f_A-1)(\alpha_A(1-v_B))^2(1-\alpha_A+\alpha_A v_B)^{f_A-2}\right] \\ & + (n_B/2)\left[(f_B\alpha_B(1-v_A))(1-(1-\alpha_B+\alpha_B v_A)^{f_B-1}) - f_B(f_B-1)(\alpha_B(1-v_A))^2(1-\alpha_B+\alpha_B v_A)^{f_B-2}\right] \end{aligned} \tag{15}$$

The concentrations of EANC's in volume unit of sol+gel, $\nu_e$, and in sol+gel, $\nu_{eg}$,

$$\nu_e = N_e \rho / M_{0n} \qquad \nu_{eg} = N_e \rho / M_{0n} w_g \tag{16}$$

where $\rho$ is specific gravity of the polymer and $M_{0n}$ is number-average molecular weight of component unit.

**Thermodynamic Stability and Solvent Activity:** The thermodynamic stability of the quasibinary (before the gel point) and quasiternary (beyond the gel point) systems will be examined in the future by calculating the spinodal and conditions for the critical point because they are a function of degree-of-polymerization averages only[12]. If phase separation occurred in system where the sol fraction is not negligible, fractionation of the sol molecules between liquid and gel phases would take place. This situation will not be examined here at present. Experiments give evidence that the system described here is one-phase until sol fraction is small; the separated liquid phase is almost a pure solvent. Therefore, solvent activity can be calculated until $a_1$ reaches unity which is the condition of phase separation for a binary gel-solvent system. From equations (2)-(5) and substituting $m_1 = 1$, $1/m_3 = 0$ and $m_2 = (V_2)_n/V_1$ ($(V_2)_n \equiv (V_s)_n$), one obtains the expression for the chemical potential of the solvent

$$\frac{\Delta\mu_1}{RT} = \ln\phi_1 + (1-m_2)\phi_2 + \phi_3 + \chi_{12}\phi_2^2 + \chi_{13}\phi_3^2 + (\chi_{12} + \chi_{13} - \frac{1}{m_2}\chi_{23})\phi_2\phi_3 + \nu_{eg}V_1[A\phi_3^{1/3}\phi_0^{2/3} - B\phi_3] \tag{17}$$

At constant $\phi_1$, the volume fractions $\phi_2$ and $\phi_3$ change with volume fraction of sol and gel are dependent on conversion as

$$\phi_2 = (1-\phi_1)\varphi_s \qquad \phi_3 = (1-\phi_1)\varphi_g$$

This corresponds to situation in closed systems. Also, the equality $\phi_3 = \phi_0$ is valid. If $\phi_1$ changes during network build-up (solvent evaporates), $\phi_0$ is an integral value over $\phi_0$-values at which EANC's were formed as shown in Ref.[1, 8]

As the composition of the polymer changes with conversion, and compositions of the sol and gel are different, the interaction parameters $\chi_{IJ}$ also change. For the present system, the change is not known, but can be estimated. What is known is the interaction parameter $\chi_{13}$ close to full conversion of functional groups (this value of $\chi_{13}$ is obtained by combination of equilibrium swelling and modulus of the swollen network). Also, we have found that in ketones $\chi_{13}$ decreases with increasing concentration of OH groups (results on off-stoichiometric systems). To get a rough estimate of the effect of conversion on the interactions, a linear dependence of interaction parameters on conversion was assumed. Thus, before the gel point

$$\chi_{12} = \chi_0 + (\chi_{13\mathrm{fin}} - \chi_0)\alpha_A \tag{18}$$

Beyond the gel point (cf., Eqs. (13) and (14))

$$\chi_{12} = \chi_0 + (\chi_{13\mathrm{fin}} - \chi_0)(\alpha_A)_s \qquad \chi_{13} = \chi_0 + (\chi_{13\mathrm{fin}} - \chi_0)(\alpha_A)_g \tag{19}$$

$\chi_{23}$ is assumed to be proportional to the difference in concentration of OH groups in sol and gel

$$\chi_{23} = \chi_{13} - \chi_{12} = (\chi_{13\mathrm{fin}} - \chi_0)[(\alpha_A)_g - (\alpha_A)_s] \tag{20}$$

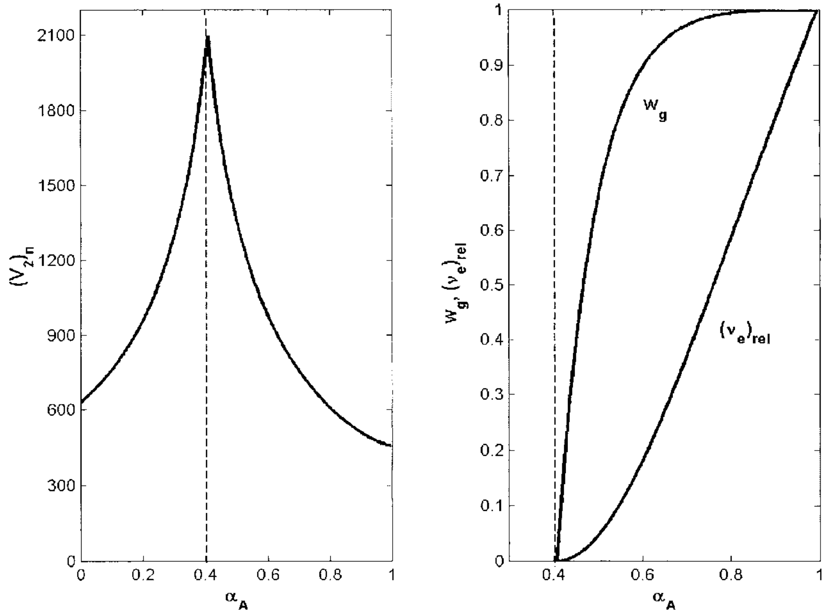

Fig. 1. Calculated dependence of number-average molar volume of sol $(V_2)_n$ [cm$^3$/mol], gel fraction $w_g$, and relative concentration of elastically active network chains [$(\nu_e)_{rel} = \nu_e(\alpha)/\nu_e(\alpha=1)$; ($\nu_e(\alpha=1) = 3.12\times10^{-3}$ mol/cm$^3$) for the system described in Experimental section with $f_A = 4$ and $f_B = 3$.

## Results and Discussion

For $f_A = 4$ and $f_B = 3$, molecular weights and molar volumes specified in the Experimental section, a number of structural parameters were calculated. The changes in number-average molar volume of the sol, $(V_2)_n$, gel fraction, $w_g$, and concentration of EANC's, $\nu_e$, are shown in Fig. 1. It is seen that the conversions of OH groups in sol, $(\alpha_A)_s$, and gel, $(\alpha_A)_g$, are different already at the gel point (Fig. 2). The number-average molar volume of sol passes through a maximum at the gel point. Close to 100%, the sol fraction is composed of initial components but their fraction is negligible (Fig. 1).

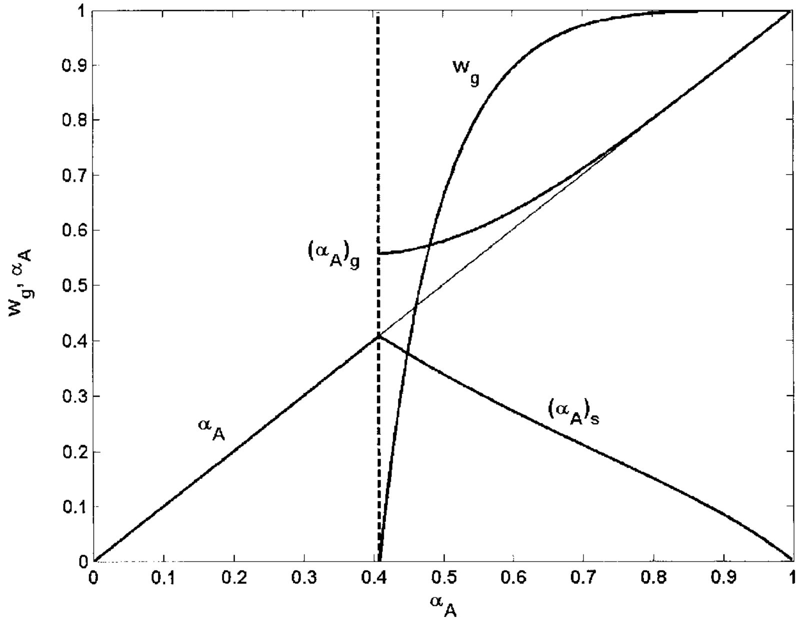

Fig. 2. Dependence of conversion of A (hydroxyl) groups in sol and gel and the gel fraction $(\alpha_A)_s$, and $(\alpha_A)_g$, respectively, on conversion for system described in Experimental section with $f_A = 4$ and $f_B = 3$.

These differences are reflected in differences in the interaction parameters $\chi_{12}$ and $\chi_{13}$ as well as non-zero value of $\chi_{23}$ (Fig. 3) estimated for methyl amyl ketone (MAK) (2-heptanone). The value of $\chi_0$ was estimated to be 0.30, and the value of $\chi_{13\text{final}} = 1.03$ (25°C) was determined experimentally by combined swelling and stress-strain measurements.

Figure 4 shows calculated dependencies of solvent activity on conversion for different concentrations of MAK valid for one-phase systems. The thermodynamic stability of the sol-gel-solvent system is not analyzed in this contribution and attention is paid mainly to the onset of solvent-gel phase separation well beyond the gel point. In this region, the condition for phase separation is given by $a_1 = 1$. The presence of the sol fraction is important just after the gel point when its molecular weight is high.

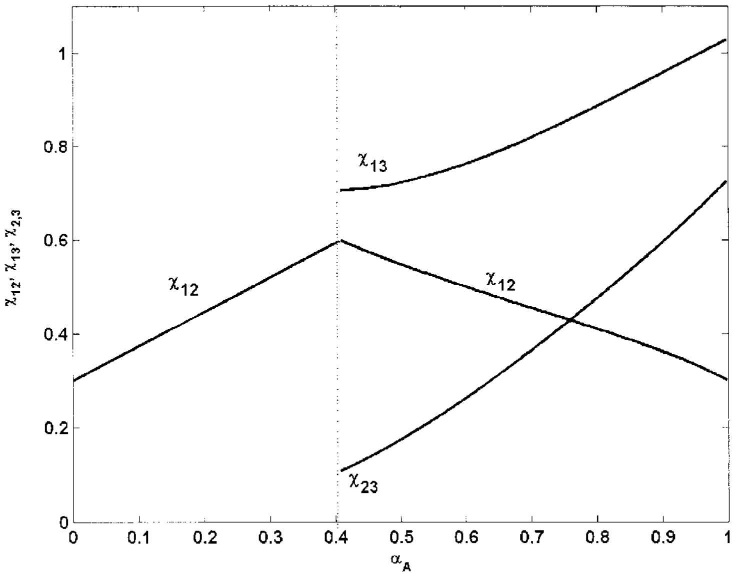

Fig. 3. Estimated change of the interaction parameters with conversion of functional groups for system described in Experimental section for interaction with methyl amyl ketone (MAK) with $f_A = 4$ and $f_B = 3$.

It can be seen that at constant solvent concentration the solvent activity increases with increasing conversion as a result of increase in both the molecular weight of the polymer before the gel point (or in crosslink density beyond the gel point) and interaction parameters $\chi_{12}$ and $\chi_{13}$. Results of direct measurements of vapor pressure over crosslinking polymer-solvent systems are not available at present. However considering vapor pressure we have indications that the increase in the activity coefficient of the solvent can compensate for the decrease in its concentration during solvent evaporation coupled with crosslinking. Thus, the solvent activity is more or less constant or even slightly increases. This tendency is seen by examining the evaporation curves for the "slow" solvent MAK expressed as increase in content of solids (or weight fraction of polymeric species) (Fig. 5).

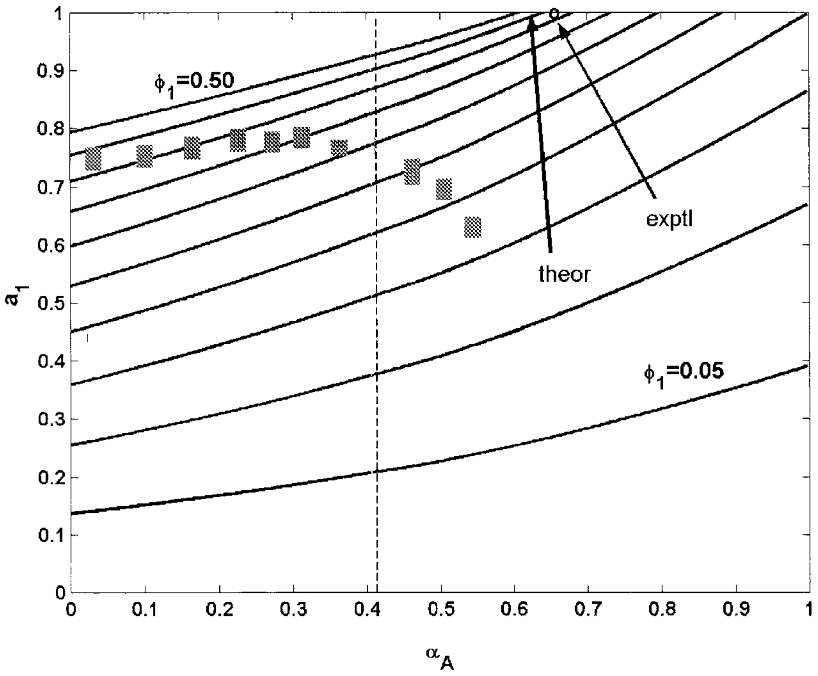

Fig. 4. Calculated dependence of solvent activity $a_1$ as a function of conversion for the polyurethane system, described in the text, at constant solvent (methyl amyl ketone) concentrations. The curves correspond to volume fraction of the solvent ranging from $\phi_1 = 0.50$ to 0.05 by steps 0.05. The bars correspond to the activity for experimental conversions and solvent contents in evaporating films shown in Fig. 5. Arrows indicate experimental and theoretical onsets of phase separation for systems containing 40 wt.-% solvent ($\phi_1 = 0.475$).

In the range of conversion up to 30-45%, the conversion of NCO groups measured in transmission (whole sample) is practically equal to that measured in the surface layer by ATR FTIR which means that the diffusion in the film is fast and the gradient in the film is not the evaporation rate determining factor. Determining the conversion and solvent content as a function of time, one can calculate from Eq. (17) in conjunction with Eqs. (9) – (16) the corresponding solvent activity as a function of conversion. The result of calculation is displayed in Fig. 4 by bars. It is seen that the solvent activity slightly increases with conversion which is consistent with the shape of evaporation curves in Fig. 5. Normally, the evaporation rate (slope of the evaporation curve) is proportional to the vapor pressure of the solvent over the film surface and would decrease with decreasing concentration of solvent in the polymer-solvent system. However, due to structure build-up and changes in thermodynamic interactions, the evaporation rate increases with decreasing concentration of the solvent in the film.

Onset of phase separation, detected experimentally by appearance of a liquid phase separated from the gel was observed in closed systems. Appearance of the liquid phase in a system containing 40 wt.-% solvent ($\phi_1$ = 0.475) was recorded repeatedly to occur at 65±3% conversion of NCO which is close to the value calculated (62%).

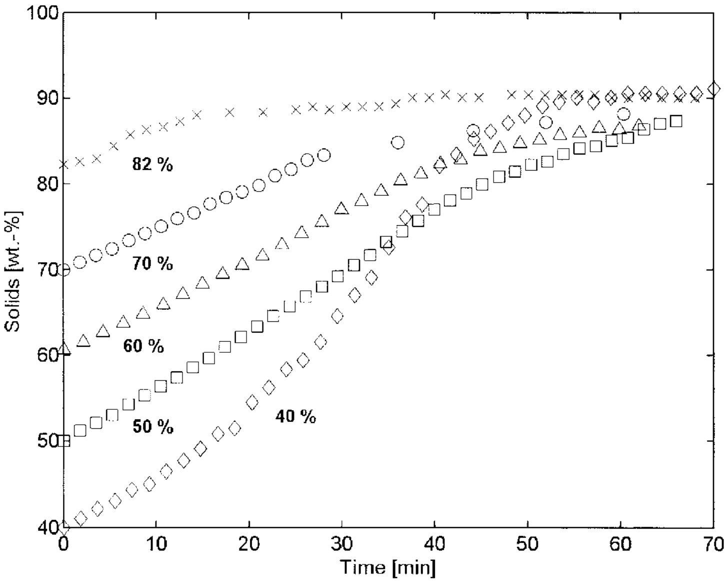

Fig. 5. Evaporation of methyl amyl ketone from films as a function of time for different initial concentration of solids in wt.-% indicated at curves; wet thickness 200μm, 200 p.p.m. catalyst (dibutyltin dilaurate), 25°C.

## Conclusions

Branching and network build-up and change in polymer solvent interactions play an important role in solvent-based coating film formation by simultaneous crosslinking and solvent evaporation. Chemical changes – consumption of functional groups and formation of bonds and increase in structure connectivity – affect the solvent activity (increase in the activity at constant solvent concentration) and assist steady evaporation. However, the danger of phase separation during film formation should be avoided. The combination of branching theory with simple thermodynamics of mixing offers a reasonable explanation of experimental observations. Theoretically, the quasiternary system solvent-sol-gel is very challenging because of coupling of branching with thermodynamics of polymer-solvent mixtures and existing singularities at the gel point.

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