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# Kinetic Modeling of Copolymerization/Cross-Linking Reactions

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ABSTRACT: A new kinetic model is developed for free radical monovinyl–divinyl monomer copolymerization/cross-linking reactions. The model includes kinetic information of the initiation, propagation and cross-linking, termination, and chain transfer to monomer steps of the polymerization. The kinetics is described in terms of the concentrations of the monovinyl, divinyl, and pendent vinyl species. The gel point, number-average molecular weight of linear polymer, and average number of cross-links per polymer chain are calculated for both the styrene/*p*-divinylbenzene and styrene/*m*-divinylbenzene reaction schemes using the moments of the molecular weight distribution of the cross-linked copolymers.

## Introduction

Copolymerization/cross-linking reactions (henceforth referred to as CCR) are typical schemes occurring in addition polymerization when a monomer with one double bond is reacted with a small amount of a monomer with two double bonds. In this case, the second monomer serves both as a comonomer in the copolymerization reaction and as the cross-linking agent. Of particular interest are reactions of a monovinyl with a divinyl monomer such as the reaction of styrene with *p*- or *m*-divinylbenzene (*p*-DVB or *m*-DVB). In this study a new kinetic model for the CCR of styrene and divinylbenzene and related monovinyl–divinyl monomer systems is presented.

The gel point, which corresponds to the formation of an infinite network, depends on the relative reactivities of the vinyl groups of the divinyl monomer and the initial cross-linking ratio, $X$, which is defined as the ratio of the divinyl to monovinyl monomer concentration. The cross-linking reaction may be intermolecular or intramolecular. Intramolecular cross-linking (cyclization, favored by the use of a transfer agent[1] or a high cross-linking ratio[2]) introduces inhomogeneities because it produces insoluble loops that are considered as gel defects.

The classical gelation theory[3,4] can be applied to monovinyl–divinyl monomer copolymerization/cross-linking reactions only in the case of equal vinyl group reactivities. Two effects give rise to deviations from this theory: the decreased reactivity of pendent vinyl groups as they are shielded by the rest of the macromolecule and the internal cyclization reactions[5]. However, this theory is not applicable to the styrene–DVB CCR because all vinyl groups do not have equal reactivities.[6-10]

Dusek[11] studied the monovinyl–divinyl monomer CCR neglecting intramolecular cyclization reactions. The calculated fraction of pendent vinyl groups for the styrene-/*p*-DVB reaction was higher than the one observed at low conversions because of the intramolecular reactions and lower than the observed one at high conversions because of the reduced segmental mobility of the polymer chains.[12] Fink[13] developed a simple model that includes intramolecular cross-linking and multiple cross-linking reactions (e.g., multiple cross-linking results in the formation of a loop between two polymer chains) for the styrene/*m*-DVB system. The classical gelation theory was used to determine the fraction of pendent vinyl groups consumed by intramolecular and multiple cross-linking reactions, which is not correct.

Most of the work done up to now has involved the study of the cross-linking kinetics up to the gel point. Before the gel point, the polymer solution viscosity is increased because of the highly branched polymer chains formed, which may cause the gel effect. After the gel point the unreacted monomers swell the polymer network and the polymerization continues within the cross-linked polymer.[14] The polymerization mechanism does not change but the observed kinetic constants do. The polymer chains are joined with each other and the polymerization steps that involve reaction of polymer chains (e.g., termination) become diffusion-controlled.[15] The diffusion of the polymer chains is segmental and not translational. The rate constants are decreased, some of them more (e.g., cross-linking and termination) and others less (e.g., propagation), and they approach zero as the reaction temperature reaches the glass transition temperature of the swollen polymer.

## Kinetic Mechanism

A set of kinetic mechanisms is presented for the monovinyl–divinyl monomer copolymerization/cross-linking reaction to calculate the molecular weight distribution of the cross-linked copolymer. The mechanism consists of four steps: initiation, propagation and cross-linking, termination by combination and disproportionation, and chain transfer to monomer. It is assumed that (i) no intramolecular cross-linking reactions take place, (ii) no depolymerization reactions occur, and (iii) the penultimate effect is negligible. The reactivities of the vinyl groups of the divinyl monomer are considered independent of each other; i.e., the reactivity of the remaining vinyl group of the divinyl monomer does not change, once one vinyl group has reacted. The kinetic modeling of copolymerization/cross-linking reactions of a monovinyl monomer with a divinyl monomer with dependent vinyl group reactivities will be discussed in another publication.

The following reaction scheme may describe all possible steps of this polymerization. In this scheme, I is the initiator, A is the initiated radical, $M_1$ is the monovinyl monomer (styrene), and $M_2$ is the divinyl monomer (divinylbenzene). We have considered primary polymer chains, that is, polymer chains which would result if all cross-links were severed.[3] The symbols $P_{p,q,r}$ and $Q_{p,q,r}$ represent living polymer chains with monovinyl and divinyl monomer terminal groups, respectively, and $M_{p,q,r}$ represents a dead polymer chain. Three subscripts are used to describe a primary chain; they correspond to the number of monovinyl units ($p$), pendent vinyl groups ($q$), and cross-links per chain ($r$).

The initiation step may include up to six reactions, including the formation of the initiated radicals, A, and its reaction with both monomers and pendent vinyl groups.

$$I \xrightarrow{k_d} 2A$$

$$M_1 + A \xrightarrow{k_{i_1}} P_{1,0,0}$$

$$M_2 + A \xrightarrow{k_{i_2}} Q_{0,1,0}$$

$$P_{p,q,r} + A \xrightarrow{k_{i_2}} P_{p,q-1,r+1} + Q_{0,0,1}$$

$$Q_{p,q,r} + A \xrightarrow{k_{i_2}} Q_{p,q-1,r+1} + Q_{0,0,1}$$

$$M_{p,q,r} + A \xrightarrow{k_{i_2}} M_{p,q-1,r+1} + Q_{0,0,1}$$

The propagation and cross-linking steps include up to ten different reactions, incorporating both reactions of monomers with propagating chains (true propagation) and reactions of longer chains with branched groups (branching and cross-linking).

$$P_{p,q,r} + M_1 \xrightarrow{k_{p_{11}}} P_{p+1,q,r}$$

$$P_{p,q,r} + M_2 \xrightarrow{k_{p_{12}}} Q_{p,q+1,r}$$

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{p_{12}}} Q_{p,q,r+1} + P_{x,y-1,z+1}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{p_{12}}} Q_{p,q,r+1} + Q_{x,y-1,z+1}$$

$$P_{p,q,r} + M_{x,y,z} \xrightarrow{k_{p_{12}}} Q_{p,q,r+1} + M_{x,y-1,z+1}$$

$$Q_{p,q,r} + M_1 \xrightarrow{k_{p_{21}}} P_{p+1,q,r}$$

$$Q_{p,q,r} + M_2 \xrightarrow{k_{p_{22}}} Q_{p,q+1,r}$$

$$Q_{p,q,r} + P_{x,y,z} \xrightarrow{k_{p_{22}}} Q_{p,q,r+1} + P_{x,y-1,z+1}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{p_{22}}} Q_{p,q,r+1} + Q_{x,y-1,z+1}$$

$$Q_{p,q,r} + M_{x,y,z} \xrightarrow{k_{p_{22}}} Q_{p,q,r+1} + M_{x,y-1,z+1}$$

It is seen that the cross-linking reaction between a growing polymer chain and a pendent vinyl group of a second polymer chain (living or dead) results in the formation of a cross-link at each chain and the reduction of a pendent vinyl group of the second chain. There are three possible termination reactions by combination.

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{tc_{11}}} M_{p+x,q+y,r+z}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{tc_{12}}} M_{p+x,q+y,r+z}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{tc_{22}}} M_{p+x,q+y,r+z}$$

There are also three possible termination reactions by disproportionation.

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{td_{11}}} M_{p,q,r} + M_{x,y,z}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{td_{12}}} M_{p,q,r} + M_{x,y,z}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{td_{22}}} M_{p,q,r} + M_{x,y,z}$$

Finally, chain transfer to the monomer can occur in CCR. It includes reactions of living polymer chains with either one of the monomers or the pendent vinyl groups. There are ten such possible reactions.

$$P_{p,q,r} + M_1 \xrightarrow{k_{f_{11}}} M_{p,q,r} + P_{1,0,0}$$

$$P_{p,q,r} + M_2 \xrightarrow{k_{f_{12}}} M_{p,q,r} + Q_{0,1,0}$$

$$P_{p,q,r} + P_{x,y,z} \xrightarrow{k_{f_{12}}} M_{p,q,r} + P_{x,y-1,z+1} + Q_{0,0,1}$$

$$P_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{f_{12}}} M_{p,q,r} + Q_{x,y-1,z+1} + Q_{0,0,1}$$

$$P_{p,q,r} + M_{x,y,z} \xrightarrow{k_{f_{12}}} M_{p,q,r} + M_{x,y-1,z+1} + Q_{0,0,1}$$

$$Q_{p,q,r} + M_1 \xrightarrow{k_{f_{21}}} M_{p,q,r} + P_{1,0,0}$$

$$Q_{p,q,r} + M_2 \xrightarrow{k_{f_{22}}} M_{p,q,r} + Q_{0,1,0}$$

$$Q_{p,q,r} + P_{x,y,z} \xrightarrow{k_{f_{22}}} M_{p,q,r} + P_{x,y-1,z+1} + Q_{0,0,1}$$

$$Q_{p,q,r} + Q_{x,y,z} \xrightarrow{k_{f_{22}}} M_{p,q,r} + Q_{x,y-1,z+1} + Q_{0,0,1}$$

$$Q_{p,q,r} + M_{x,y,z} \xrightarrow{k_{f_{22}}} M_{p,q,r} + M_{x,y-1,z+1} + Q_{0,0,1}$$

This completes the formal development of the kinetic model.

## Molecular Weight Distribution

The rate equations for the concentrations of the various polymerizing species and the moments of the molecular weight distribution of the cross-linked copolymer resulting from the proposed mechanism may be written as follows:

Initiator I

$$r_{\mathrm{I}} = -k_{\mathrm{d}}I \tag{1}$$

Initiated radical A

$$r_{\mathrm{A}} = 2fk_{\mathrm{d}}I - [k_{i_1}M_1 + k_{i_2}(2M_2 + M_3)]A \tag{2}$$

Here, $M_3$ is the concentration of pendent vinyl groups, defined as

$$M_3 \equiv \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} q(P_{p,q,r} + Q_{p,q,r} + M_{p,q,r}) \tag{3}$$

Monovinyl monomer $M_1$

$$r_{M_1} = -[k_{i_1}A + (k_{p_{11}} + k_{f_{11}})P + (k_{p_{21}} + k_{f_{21}})Q]M_1 \tag{4}$$

The terms $P$ and $Q$ are the concentrations of total living polymer with monovinyl and divinyl monomer terminals, respectively. These terms are defined by eq 5 and 6.

$$P \equiv \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} P_{p,q,r} \tag{5}$$

$$Q \equiv \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty} Q_{p,q,r} \tag{6}$$

Divinyl monomer $M_2$

$$r_{M_2} = -2[k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q]M_2 \tag{7}$$

Living polymer $P_{p,q,r}$

$$\begin{aligned} r_{P_{p,q,r}} = {} & (k_{p_{11}}P_{p-1,q,r} + k_{p_{21}}Q_{p-1,q,r})M_1 - [k_{i_2}A + (k_{p_{12}} + \\ & k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q][qP_{p,q,r} - (q+1)P_{p,q+1,r-1}] - \\ & [(k_{p_{11}} + k_{f_{11}})M_1 + (k_{p_{12}} + k_{f_{12}})(2M_2 + M_3) + \\ & (k_{tc_{11}} + k_{td_{11}})P + (k_{tc_{12}} + k_{td_{12}})Q]P_{p,q,r} \end{aligned} \tag{8}$$

Total living polymer P

$$\begin{aligned} r_{\mathrm{P}} = {} & \\ & [k_{i_1}A + (k_{p_{21}} + k_{f_{21}})Q]M_1 - [(k_{p_{12}} + k_{f_{12}})(2M_2 + M_3) + \\ & (k_{tc_{11}} + k_{td_{11}})P + (k_{tc_{12}} + k_{td_{12}})Q]P \end{aligned} \tag{9}$$

Living polymer $Q_{p,q,r}$

$$\begin{aligned} r_{Q_{p,q,r}} = {} & 2(k_{p_{12}}P_{p,q-1,r} + k_{p_{22}}Q_{p,q-1,r})M_2 + (k_{p_{12}}P_{p,q,r-1} + k_{p_{22}}Q_{p,q,r-1})M_3 - [k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + \\ & (k_{p_{22}} + k_{f_{22}})Q][qQ_{p,q,r} - (q+1)Q_{p,q+1,r-1}] - [(k_{p_{21}} + k_{f_{21}})M_1 + (k_{p_{22}} + k_{f_{22}})(2M_2 + M_3) + \\ & (k_{tc_{12}} + k_{td_{12}})P + (k_{tc_{22}} + k_{td_{22}})Q]Q_{p,q,r} \end{aligned} \quad (10)$$

Total living polymer Q

$$\begin{aligned} r_Q = {} & [k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P](2M_2 + M_3) - \\ & [(k_{p_{21}} + k_{f_{21}})M_1 + (k_{tc_{12}} + k_{td_{12}})P + (k_{tc_{22}} + k_{td_{22}})Q]Q \end{aligned} \quad (11)$$

Dead polymer $M_{p,q,r}$

$$\begin{aligned} r_{M_{p,q,r}} = {} & [k_{f_{11}}M_1 + k_{f_{12}}(2M_2 + M_3)]P_{p,q,r} + [k_{f_{21}}M_1 + k_{f_{22}}(2M_2 + M_3)]Q_{p,q,r} - [k_{i_2}A + (k_{p_{12}} + \\ & k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q][qM_{p,q,r} - (q+1)M_{p,q+1,r-1}] + \tfrac{1}{2}k_{tc_{11}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}P_{x,y,z}P_{p-x,q-y,r-z} + \\ & k_{tc_{12}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{z=0}^{r}P_{x,y,z}Q_{p-x,q-y,r-z} + \tfrac{1}{2}k_{tc_{22}}\sum_{x=0}^{p}\sum_{y=0}^{q}\sum_{x=0}^{r}Q_{x,y,z}Q_{p-x,q-y,r-z} + \\ & (k_{td_{11}}P + k_{td_{12}}Q)P_{p,q,r} + (k_{td_{12}}P + k_{td_{22}}Q)Q_{p,q,r} \end{aligned} \quad (12)$$

The moments of the molecular weight distribution, $\psi_{i,j,k}$, of cross-linked copolymer for the total polymer are defined as follows:

$$\psi_{i,j,k} \equiv \sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\sum_{r=0}^{\infty}p^i q^j r^k (P_{p,q,r} + Q_{p,q,r} + M_{p,q,r}) \quad (13)$$

where $i$, $j$, and $k$ are integers. By definition

$$\psi_{0,1,0} \equiv M_3 \quad (14)$$

On the basis of the definition of the distribution moments, some of the rate equations may be now constructed. The rate equation for the concentration of total polymer is

$$\begin{aligned} r_{\psi_{0,0,0}} = {} & [k_{i_1}M_1 + k_{i_2}(2M_2 + M_3)]A - \tfrac{1}{2}k_{tc_{11}}P^2 - k_{tc_{12}}PQ - \tfrac{1}{2}k_{tc_{22}}Q^2 + [k_{f_{11}}M_1 + k_{f_{12}}(2M_2 + M_3)]P + \\ & [k_{f_{21}}M_1 + k_{f_{22}}(2M_2 + M_3)]Q \end{aligned} \quad (15)$$

The rate equation for the concentration of monovinyl units in the polymer is

$$r_{\psi_{1,0,0}} = [k_{i_1}A + (k_{p_{11}} + k_{f_{11}})P + (k_{p_{21}} + k_{f_{21}})Q]M_1 \quad (16)$$

The rate equation for the concentration of pendent vinyl groups in the polymer is

$$r_{\psi_{0,1,0}} = [k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q](2M_2 - M_3) \quad (17)$$

Finally, the rate equation for the concentration of cross-links is

$$r_{\psi_{0,0,1}} = 2[k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q]M_3 \quad (18)$$

Invoking now the quasi-steady-state approximation for the initiated radical, A, we obtain

$$[k_{i_1}M_1 + k_{i_2}(2M_2 + M_3)]A = 2fk_dI \quad (19)$$

Thus, eq 15 becomes

$$\begin{aligned} r_{\psi_{0,0,0}} = {} & 2fk_dI - \tfrac{1}{2}k_{tc_{11}}P^2 - k_{tc_{12}}PQ - \tfrac{1}{2}k_{tc_{22}}Q^2 + [k_{f_{11}}M_1 + \\ & k_{f_{12}}(2M_2 + M_3)]P + [k_{f_{21}}M_1 + k_{f_{22}}(2M_2 + M_3)]Q \end{aligned} \quad (20)$$

The moments of the molecular weight distribution of the cross-linked copolymer are used to evaluate important averages such as the number-average molecular weight (linear polymer) ($\bar{M}_n$) and the number-average molecular weight between cross-links ($\bar{M}_c$). The equations are

$$\bar{M}_n = \frac{w_1\psi_{1,0,0} + w_2(\psi_{0,1,0} + \tfrac{1}{2}\psi_{0,0,1})}{\psi_{0,0,0}} \quad (21)$$

$$\bar{M}_c = \bar{M}_n/(1 + \nu_e) \quad (22)$$

Here, $w_1$ and $w_2$ are the molecular weights of the monovinyl and divinyl monomer, respectively, and $\nu_e$ is the average number of effective cross-links per chain (i.e., the cross-links resulting from intermolecular cross-linking reactions) given by

$$\nu_e = \psi_{0,0,1}/\psi_{0,0,0} \quad (23)$$

## Gelation

The gel point corresponds to the incipient formation of an infinite network. Before the gel point all the polymerization steps may be assumed reaction-controlled (no gel effect), which implies that the reaction rate constants are indeed constant. After the gel point this assumption is not valid for the cross-linking, the termination, and chain transfer to pendent vinyl group steps, as they become diffusion-controlled.

The gel point can be calculated by using the proposed kinetic model. It corresponds to an average number of effective cross-links per (linear) chain equal to two.

$$\nu_e = \psi_{0,0,1}/\psi_{0,0,0} = 2 \quad (24)$$

Beyond the gel point the polymerization rate constants of the diffusion-controlled steps change. This change can be described by a mobility factor, $\mu$, defined as

$$\mu = \frac{\text{polymerization rate of cross-linked chains}}{\text{polymerization rate of primary chains}} \quad (25)$$

The mobility factor depends on the mobility of the cross-linked chains and is a function of the average number of cross-links per chain, $\nu_e$.

$$\nu = \mu(\nu_e) \quad (26)$$

Cardenas and O'Driscoll[16] developed a kinetic model for the polymerization of methyl methacrylate at high conversions assuming that the termination rate constant for entangled chains with radicals is inversely proportional to the entanglement density. Since entanglements may be considered as physical cross-links and therefore similar to chemical cross-links in terms of restricting chain mobility, we postulate, by analogy to their work, that the mobility factor, $\mu$, is inversely proportional to the average number of crosslinks per chain, $\nu_e$.

$$\mu = c/\nu_e \quad (27)$$

The proportionality constant $c$ may be regarded as a model parameter and it will depend on the solvent content if solution polymerization is utilized.

Consequently, the rate equations for the distribution moments of total polymer are modified for the reaction period after gelation to yield

$$\begin{aligned} r_{\psi_{0,0,0}} = {} & 2fk_dI - \mu(\tfrac{1}{2}k_{tc_{11}}P^2 + k_{tc_{12}}PQ + \tfrac{1}{2}k_{tc_{22}}Q^2) + \\ & [k_{f_{11}}M_1 + k_{f_{12}}(2M_2 + \mu M_3)]P + [k_{f_{21}}M_1 + k_{f_{22}}(2M_2 + \mu M_3)]Q \end{aligned} \quad (28)$$

$$r_{\psi_{0,1,0}} = [k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q](2M_2 - \mu M_3) \quad (29)$$

and

$$r_{\psi_{0,0,1}} = 2[k_{i_2}A + (k_{p_{12}} + k_{f_{12}})P + (k_{p_{22}} + k_{f_{22}})Q]\mu M_3 \qquad (30)$$

## Vitrification

The polymerization reaction ceases either at total conversion or at vitrification. Vitrification is defined as the transition from the liquid phase (or rubbery state) to the glassy state of the amorphous phase, which can occur before or after the gel point. At the glass transition temperature the monomer diffusion coefficient falls approximately 4 orders of magnitude.[17] This results essentially in the cessation of the polymerization reaction. Therefore, the cessation of the polymerization reaction is not necessarily an indication of total conversion.

The condition for vitrification is that the reaction temperature, $T$, be equal to the glass transition temperature of the polymer system, $T_g$, i.e., the highly entangled polymer "solution" or the swollen gel, depending on whether vitrification occurs before or after gelation, respectively. The glass transition temperature of the polymer system, assuming free volume additivity, may be written[18] as

$$T_g = \frac{\alpha_1 v_1 T_{g_1} + \alpha_2 v_2 T_{g_2} + \alpha_p(1 - v_1 - v_2)T_{g_p}}{\alpha_1 v_1 + \alpha_2 v_2 + \alpha_p(1 - v_1 - v_2)} \qquad (31)$$

Here, the term $\alpha$ is the difference between the volume expansion coefficients of the liquid phase (or rubbery state) and the glassy state, $v$ is the volume fraction, and the subscripts 1, 2, and p refer to monovinyl monomer, divinyl monomer, and polymer, respectively. The volume fractions of these components are given by

$$v_1 = \frac{M_1 w_1/\rho_1}{M_1 w_1(1/\rho_1 - 1/\rho_p) + M_2 w_2(1/\rho_2 - 1/\rho_p) + \rho/\rho_p} \qquad (32)$$

$$v_2 = \frac{M_2 w_2/\rho_2}{M_1 w_1(1/\rho_1 - 1/\rho_p) + M_2 w_2(1/\rho_2 - 1/\rho_p) + \rho/\rho_p} \qquad (33)$$

$$v_p = 1 - v_1 - v_2 \qquad (34)$$

Before gelation the polymer consists of a mixture of linear and branched macromolecules. The glass transition temperature of the polymer may be approximated to that of the linear copolymer, that is, as a weighted average of the glass transition temperatures of the homopolymers.

The glass transition temperature of the cross-linked polymer increases with degree of cross-linking.[19] The shift in the glass transition temperature is also caused by the copolymer effect.[20] Thus, for the styrene–divinylbenzene system it can be related to the degree of cross-linking through

$$\frac{T_{g_p} - T_{g_p}'}{T_{g_p}'} \simeq 1.2\frac{\psi_{0,0,1}}{\psi_{1,0,0} + \psi_{0,1,0}} \qquad (35)$$

Here $T_{g_p}'$ is the glass transition temperature of the linear copolymer (in the absence of cross-links). It must be noted that only if the cross-linking ratio is small can the glass transition temperature of the linear copolymer, $T_{g_p}'$, be approximated with the glass transition temperature of the homopolymer corresponding to the monovinyl monomer.

**Table I**
**Kinetic Constants for the Styrene–Divinylbenzene Copolymerization/Cross-Linking Reaction**

| kinetic constants | ref |
|---|---|
| $k_d = 6.38 \times 10^{13} \exp(-29.7 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$ | 21 |
| $k_{p11} = 1.06 \times 10^7 \exp(-7.07 \text{ kcal mol}^{-1}/RT) \text{ L mol}^{-1} \text{ s}^{-1}$ | 21 |
| $k_{f_{11}} = 2.33 \times 10^6 \exp(-12.67 \text{ kcal mol}^{-1}/RT) \text{ L mol}^{-1} \text{ s}^{-1}$ | 21 |
| $k_{tc_{11}} = 1.26 \times 10^9 \exp(-1.68 \text{ kcal mol}^{-1}/RT) \text{ L mol}^{-1} \text{ s}^{-1}$ | 21 |
| $k_{td_{11}} = 0$ | 22 |
| $r_1 = 1.11$, $r_2 = 1.00$ (styrene/*m*-DVB) | 10 |
| $r_1 = 0.20$, $r_2 = 1.00$ (styrene/*p*-DVB) | 10 |

## Reaction Engineering

The developed kinetic model is solved for a batch isothermal polymerization reactor. The mass balance equations for the initiator, both monomers, and the distribution moments of the cross-linked copolymer are given by

$$\frac{dI}{dt} + \frac{I}{v}\frac{dv}{dt} = r_I; \qquad I(0) = I_0 \qquad (36)$$

$$\frac{dM_1}{dt} + \frac{M_1}{v}\frac{dv}{dt} = r_{M_1}; \qquad M_1(0) = M_{1_0} \qquad (37)$$

$$\frac{dM_2}{dt} + \frac{M_2}{v}\frac{dv}{dt} = r_{M_2}; \qquad M_2(0) = M_{2_0} \qquad (38)$$

$$\frac{d\psi_{i,j,k}}{dt} + \frac{\psi_{i,j,k}}{v}\frac{dv}{dt} = r_{\psi_{i,j,k}}; \qquad \psi_{i,j,k}(0) = 0 \qquad (39)$$

The reactor volume, $v$, changes during the polymerization because the polymer density, $\rho_p$, differs from those of the monovinyl and divinyl monomers, $\rho_1$ and $\rho_2$, respectively. The rate of volume change, assuming volume additivity and neglecting the volume of the initiator, is

$$\frac{dv}{dt} = \left[r_{M_1}w_1\left(\frac{1}{\rho_1} - \frac{1}{\rho_p}\right) + r_{M_2}w_2\left(\frac{1}{\rho_2} - \frac{1}{\rho_p}\right)\right]v \qquad (40)$$

## Results and Discussion

The kinetic model for the monovinyl–divinyl monomer copolymerization/cross-linking reaction is solved for the styrene/*p*-DVB and styrene/*m*-DVB systems using benzoyl peroxide as an initiator. In order to solve the material balance equations the quasi-steady state approximation is invoked for the total living polymer with a styrene terminal, P, and the total living polymer with a divinylbenzene terminal, Q.

$$r_P = 0 \qquad (41)$$

$$r_Q = 0 \qquad (42)$$

Assuming also that the propagation rates are much larger than both the initiation and termination rates from eq 9, 11, and 19 we get

$$P = \left(\frac{2fk_dI}{(k_{tc_{11}} + k_{td_{11}}) + 2a(k_{tc_{12}} + k_{td_{12}}) + a^2(k_{tc_{22}} + k_{td_{22}})}\right)^{1/2} \qquad (43)$$

$$Q = aP \qquad (44)$$

The parameter $a$ appearing in both equations is defined as

$$a = \frac{(k_{p_{12}} + k_{f_{12}})(2M_2 + M_3)}{(k_{p_{21}} + k_{f_{21}})M_1} \qquad (45)$$

The values of the kinetic constants are presented in Table I. The free volume constants used in the calculations[19] are $T_{g_p} = 100$ °C, $\alpha_p = 5.5 \times 10^{-4}$ K$^{-1}$, $\alpha_1 = 11.7 \times 10^{-4}$ K$^{-1}$. The monomer glass transition temperatures are assumed as $T_{g_1} = T_{g_2} = -100$ °C by analogy to related

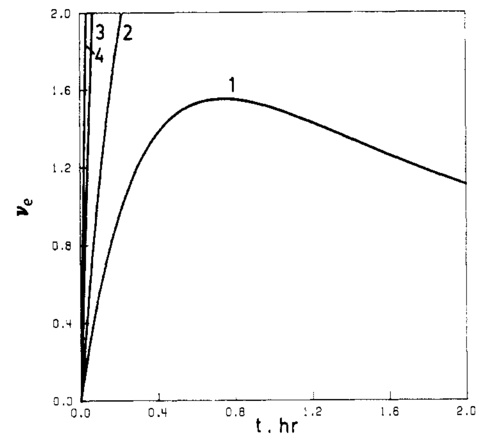

**Figure 1.** Effect of the cross-linking ratio, $X$, on the number of effective cross-links per chain, $\nu_e$, up to the gel point for the reaction of styrene and $p$-DVB at 85 °C using an initiator concentration of $I_0$ = 0.1 mol/L. Four different cross-linking ratios were used: $X$ = 0.001 (curve 1), $X$ = 0.002 (curve 2), $X$ = 0.005 (curve 3), and $X$ = 0.010 (curve 4).

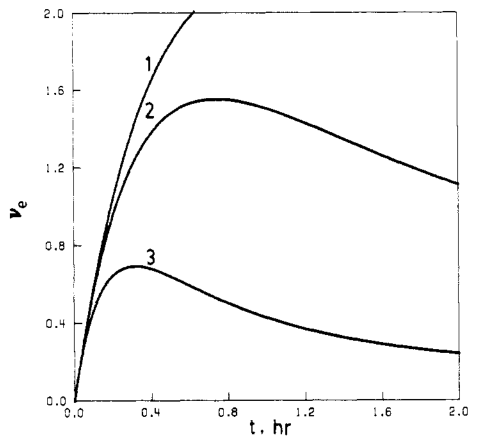

**Figure 2.** Effect of the initial concentration of the initiator, $I_0$, on the number of effective cross-links per chain, $\nu_e$, up to the gel point for the reaction of styrene and $p$-DVB at 85 °C using a cross-linking ratio of $X$ = 0.001. Three different initiator concentrations were used: $I_0$ = 0.05 mol/L (curve 1), $I_0$ = 0.1 mol/L (curve 2), and $I_0$ = 0.5 mol/L (curve 3).

monomers and $\alpha_2 = 11.7 \times 10^{-4}$ K$^{-1}$. For the solution of the model the following reasonable approximations were also made: (i) The initiator efficiency is 0.5. (ii) The propagation constants for cross polymerization are equal; i.e., $k_{p_{12}} = k_{p_{21}}$. (iii) The reactivity ratios, $r_1$ and $r_2$, are temperature-independent in the temperature range from 75 to 95 °C. They refer to the double bonds of the divinyl compound and not to the compound itself. The values reported by Wiley et al.[10] are used, because they are averaged values at high conversions and therefore, as stated, more accurate than those reported at low conversions. (iv) The chain-transfer constants are equal to each other; i.e., $k_{f_{11}} = k_{f_{12}} = k_{f_{21}} = k_{f_{22}}$. (v) The termination by combination constants are equal to each other; i.e., $k_{tc_{11}} = k_{tc_{12}} = k_{tc_{22}}$. (vi) The termination by disproportionation constants are equal to each other; i.e., $k_{td_{11}} = k_{td_{12}} = k_{td_{22}}$. The mass balance equations for the initiator, the monovinyl monomer, and the divinyl monomer, and the zero and the first distribution moments of the molecular weight distribution of the cross-linked copolymer constitute a system of ordinary differential equations solved numerically by the Adams method.

**Studies before Gelation.** Data are presented first of the effect of the cross-linking ratio, that is, the molar ratio of DVB to styrene, on the number of effective cross-links per chain, $\nu_e$, and on the gelation time. Figure 1 shows this dependence for a reaction of styrene and $p$-DVB occurring at 85 °C and initiated with 0.1 mol of initiator per liter of solution, when the cross-linking ratio varies from 0.001 to 0.010. As the reaction time increases, the value of $\nu_e$ increases for most cases up to the gelation, which occurs at $\nu_e$ = 2. The time corresponding to this value is the gelation time. Thus, as the cross-linking ratio, $X$, increases from 0.002 to 0.010 the gelation time decreases from 14 to 2 min. However, for an initial cross-linking ratio of $X$ = 0.001 no gelation occurs. Instead, the value of $\nu_e$ passes through a maximum below the gel point. The absence of gelation point is due to insufficient concentration of the cross-linking agent ($p$-DVB). In this case the final product is a mixture of branched macromolecules and the value of $\nu_e$ represents the average number of branches per primary chain. Similar results were obtained for the reaction of styrene with $m$-DVB.

The effect of the initial concentration of the initiator on the average number of effective cross-links and the gelation time is shown in Figure 2 for the styrene/$p$-DVB reaction at 85 °C for a cross-linking ratio of 0.001. As the reaction time increases, $\nu_e$ increases up to 2 for initiator concentration of $I_0$ = 0.05 mol/L. However, for the values of the initial concentration of the initiator of 0.1 and 0.5 mol/L the number of cross-links passes through a maximum below the value $\nu_e$ = 2; for these values gelation is not attained. This happens because as the initial concentration of the initiator increases, the number of initiated radicals formed in the initiation step also increases, resulting in an increase of the polymer concentration. Therefore, gelation may not occur either because the concentration of the cross-linking agent is insufficient to render all polymer chains joined or because of high initial concentrations of the initiator.

The temperature dependence of the average number of effective cross-links is shown in Figure 3a for the styrene/$m$-DVB reaction for a cross-linking ratio equal to 0.010 and an initial concentration of the initiator of 0.1 mol/L. As the temperature increases, the number of cross-links increases due to elevated cross-linking rates. The gelation time changes from 118 to 65 min as the temperature increases from 75 to 95 °C. Nevertheless, high temperatures do not always result in high number of cross-links and small gelation times, as shown in Figure 3b for the styrene/$p$-DVB reaction. Although initially $\nu_e$ increases faster at higher temperatures, a maximum value of the number of cross-links is observed for temperatures of 85 and 95 °C, since at high temperatures the initiation rate increases in addition to the cross-linking rate and, as previously discussed, high initiation rates result in high concentrations of polymer chains.

The effect of the type of cross-linking agent on the average number of effective cross-links is shown in Figure 4 for the copolymerization/cross-linking reaction of styrene and DVB. Under the same reaction conditions the number of cross-links increases faster with $p$-DVB rather than $m$-DVB as a cross-linking agent. The gelation time for reaction with $p$-DVB (2 min) is much faster than that for $m$-DVB (82 min). Low cross-linking ratios result in low fractions of living polymer chains with a divinyl monomer terminal unit according to eq 44 and 45. Therefore, the calculated results are not sensitive to the reactivity ratio $r_2$, if $k_{p_{12}}$ and $k_{p_{21}}$ are of the same order of magnitude and the chain transfer to monomer rate constants are much smaller than the propagation constants (Table I). The polymer chains with a monovinyl monomer terminal unit predominate at low cross-linking ratios. Small values of $r_1$ result in slower incorporation of monovinyl monomer

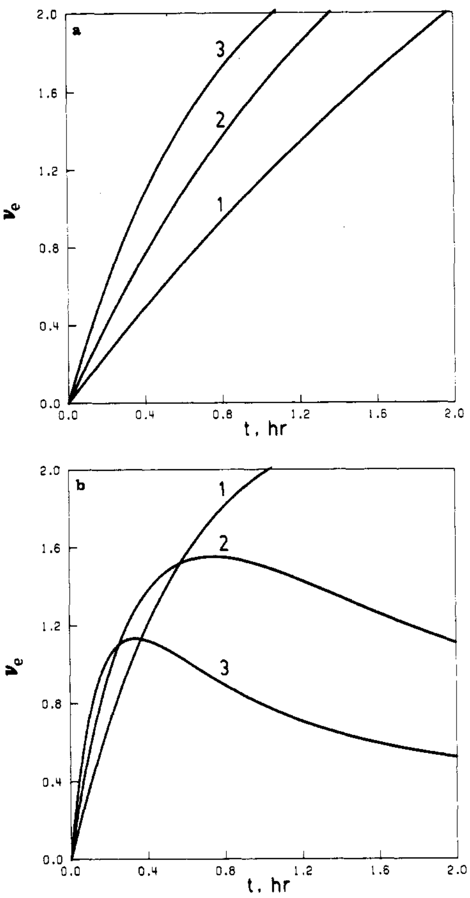

**Figure 3.** Effect of the reaction temperature, $T$, on the number of effective cross-links per chain, $\nu_e$, up to the gel point for the reaction of styrene with (a) *m*-DVB using a cross-linking ratio of $X = 0.010$ and (b) *p*-DVB using a cross-linking ratio of $X = 0.001$. The initiator concentration, $I_0$ was 0.1 mol/L. Three different temperatures were used: $T = 75$ °C (curve 1), $T = 85$ °C (curve 2), and $T = 95$ °C (curve 3).

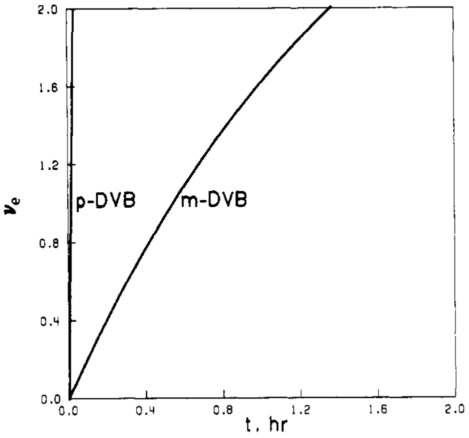

**Figure 4.** Effect of the type of the divinyl monomer (cross-linking agent) on the number of effective cross-links per chain, $\nu_e$, up to the gel point for the reaction with styrene at 85 °C using a cross-linking ratio of $X = 0.010$ and an initiator concentration of $I_0 = 0.1$ mol/L.

units into the polymer chains rather than that of the cross-linking agent. Thus, gelation happens faster in the styrene/*p*-DVB reaction than in the styrene/*m*-DVB reaction, based on the corresponding values of $r_1$ ($r_1 = 0.20$ for *p*-DVB; $r_1 = 1.11$ for *m*-DVB).

**Studies after Gelation.** For simulations beyond the gel point, the mobility factor is introduced, as defined in eq 25. The proportionality constant $c$ is assumed equal to 1. The rate equations for the zero and the first distribution moments are given in eq 16, 28, 29, and 30. The concentrations of total living polymer with styrene and divinylbenzene terminal group, eq 43–45, are also modified as follows:

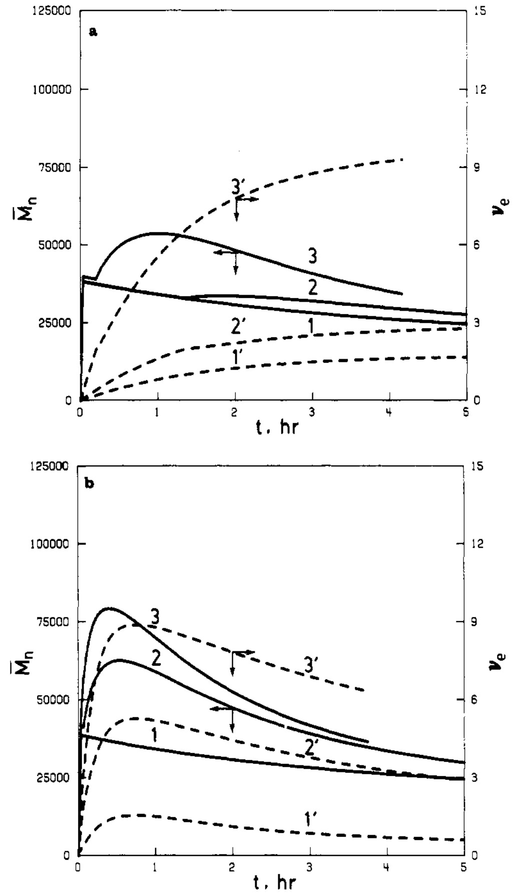

**Figure 5.** Effect of the cross-linking ratio, $X$, on the number-average molecular weight, $\bar{M}_n$ (curves 1, 2, and 3), and the average number of effective cross-links per chain, $\nu_e$ (curves 1′, 2′, and 3′), during the reaction of styrene with (a) *m*-DVB and (b) *p*-DVB at 85 °C using an initiator concentration of $I_0 = 0.1$ mol/L. Three cross-linking ratios were used: (a) $X = 0.005$ (curves 1 and 1′), $X = 0.010$ (curves 2 and 2′), and $X = 0.050$ (curves 3 and 3′); (b) $X = 0.001$ (curves 1 and 1′), $X = 0.005$ (curves 2 and 2′), and $X = 0.010$ (curves 3 and 3′).

$$P = \left( \frac{2fk_dI}{[(k_{tc_{11}} + k_{td_{11}}) + 2a'(k_{tc_{12}} + k_{td_{12}}) + a'^2(k_{tc_{22}} + k_{td_{22}})]\mu} \right)^{1/2} \tag{46}$$

$$Q = a'P \tag{47}$$

where

$$a' = \frac{(k_{p_{12}} + k_{f_{12}})(2M_2 + \mu M_3)}{(k_{p_{21}} + k_{f_{21}})M_1} \tag{48}$$

The effect of the cross-linking ratio, $X$, on the number-average molecular weight, $\bar{M}_n$, and the average number of effective cross-links per polymer chain, $\nu_e$, is shown in Figure 5a for the cross-linked polystyrene produced from the reaction of styrene with *m*-DVB as a cross-linking agent at 85 °C for an initial concentration of the initiator of 0.1 mol/L. Gelation is not observed for $X = 0.005$ because of the insufficient concentration of the cross-linking agent. In this case the values of $\bar{M}_n$ and $\nu_e$ corre-

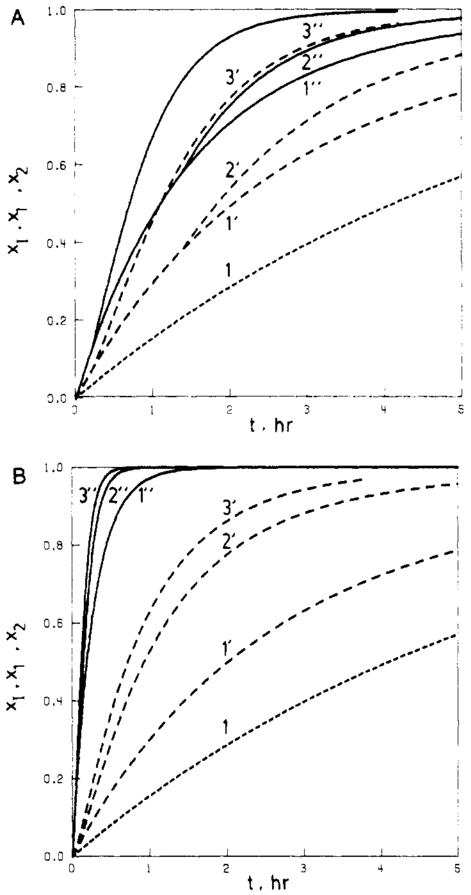

**Figure 6.** Effect of the cross-linking ratio, $X$, on the conversion of the initiator, $x_I$ (curve 1), styrene, $x_1$ (curves 1′, 2′, and 3′), and $m$-DVB, $x_2$ (curves 1″, 2″, and 3″), during the reaction of styrene with (A) $m$-DVB and (B) $p$-DVB at 85 °C using an initiator concentration of $I_0 = 0.1$ mol/L. Three cross-linking ratios were used: (A) $X = 0.005$ (curves 1, 1′, and 1″), $X = 0.010$ (curves 2, 2′, and 2″), and $X = 0.050$ (curves 1, 3′, and 3″); (B) $X = 0.001$ (curves 1, 1′, and 1″), $X = 0.005$ (curves 1, 2′, and 2″), and $X = 0.010$ (curves 1, 3′, and 3″).

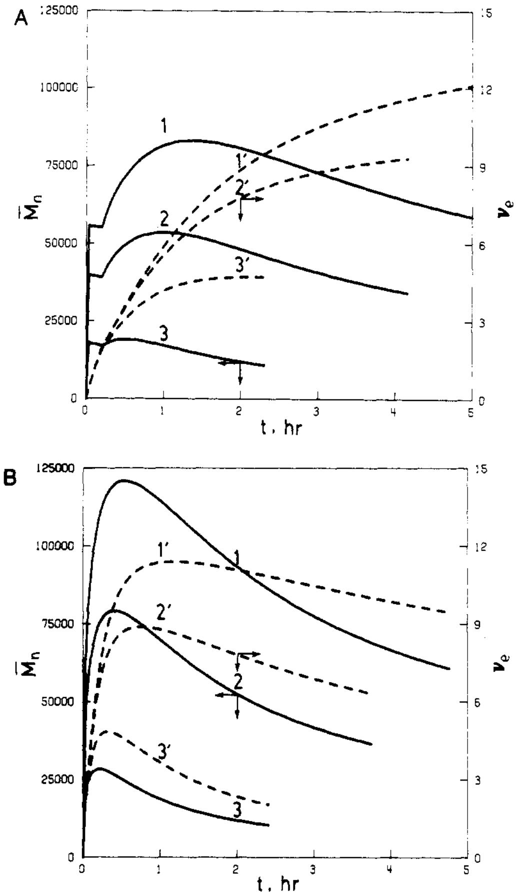

**Figure 7.** Effect of the initial concentration of the initiator, $I_0$, on the number-average molecular weight, $\bar{M}_n$ (curves 1, 2, and 3), and the average number of effective cross-links per chain, $\nu_e$ (curves 1′, and 2′, and 3′), during the reaction of styrene with (A) $m$-DVB of $X = 0.050$ and (B) $p$-DVB using a cross-linking ratio of $X = 0.010$ at 85 °C. Three different initiator concentrations were used: $I_0 = 0.05$ mol/L (curves 1 and 1′), $I_0 = 0.1$ mol/L (curves 2 and 2′), and $I_0 = 0.5$ mol/L (curves 3 and 3′).

spond to the average molecular weight of the branched polymer and the average number of branches per polymer chain.

Gelation occurs after 82 and 13 min for cross-linking ratios of 0.010 and 0.050, respectively. The value of $\bar{M}_n$ initially decreases until the gel point, where it increases abruptly to a maximum value, which is apparent for $X = 0.050$. The change of the average molecular weight depends on the relative magnitude of the initiation, propagation, and termination reaction rates.

The rate of change of $\nu_e$ decreases after the gel point due to production of large polymer chains. For a reaction with a cross-linking ratio of 0.050 the reaction ceases after 4.17 h, because at that point the reaction temperature becomes equal to the glass transition temperature of the swollen polymer (i.e., vitrification point). For cross-linking ratios of 0.005 and 0.010 the gelation time is so small for the styrene/$p$-DVB reaction (Figure 5b) that the abrupt change in the molecular weight, corresponding to the gel point, is not obvious. The average number of effective cross-links passes through a maximum and then decreases, due to sudden formation of high molecular weight polymer chains at the gel point.

Before gelation, the average molecular weight of linear polymer (Figure 5a) and the monomer conversions (Figure 6a) are not affected much by the cross-linking ratio. Because of the small values of the cross-linking agent, the copolymerization/cross-linking reaction is similar to the homopolymerization reaction. However, after gelation the termination rate is decreased, resulting in an abrupt change of the molecular weight at the gel point. Besides, the monomer conversions are increased after gelation because the decreased termination rate favors the propagation step. Also, as the cross-linking ratio increases, the average number of effective cross-links also increases.

For a cross-linking ratio of 0.010 the reaction ceases after 3.75 h due to vitrification. High cross-linking ratios result in high monomer conversions as shown in Figure 6. The role of unreacted monomers as plasticizers diminishes, causing cessation of the polymerization due to vitrification. The reader should recall that the unreacted monomers are plasticizers for the polymer and lower its glass transition temperature (eq 31). Finally, the initiator conversion depends only on the temperature, as shown in eq 1.

The effect of the initial concentration of the initiator on $\bar{M}_n$ and $\nu_e$ is shown in Figure 7A for the styrene/$m$-DVB scheme at 85 °C for a cross-linking ratio of 0.050. The molecular weight and the number of cross-links decrease as the initiator concentration changes from 0.05 to 0.5 mol/L because of the increased polymer concentration. Again, for the styrene/$m$-DVB reaction the abrupt change in the molecular weight at the gel point is obvious in contrast with the styrene/$p$-DVB system (Figure 7B) because of the very small gelation times.

As previously discussed, the higher the initial concentration of the initiator, the higher the concentration of the initiated radicals formed, which implies that the monomer

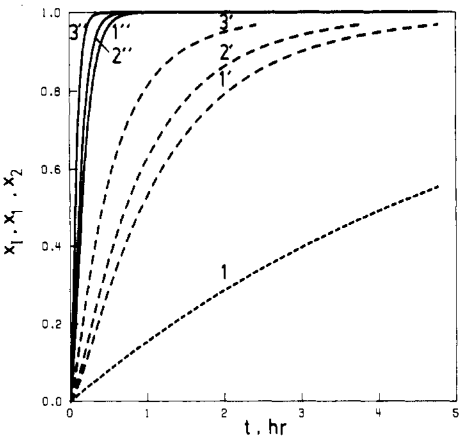

**Figure 8.** Effect of the initial concentration of the initiator, $I_0$, on the conversion of the initiator, $x_I$ (curve 1), styrene, $x_1$ (curves 1', 2', and 3'), and *p*-DVB, $x_2$ (curves 1'', 2'', and 3''), during the reaction of styrene and *p*-DVB at 85 °C using a cross-linking ratio of $X = 0.010$. Three different initiator concentrations were used: $I_0 = 0.05$ mol/L (curves 1, 1', and 1''), $I_0 = 0.1$ mol/L (curves 1, 2', and 2''), and $I_0 = 0.5$ mol/L (curves 1, 3', and 3'').

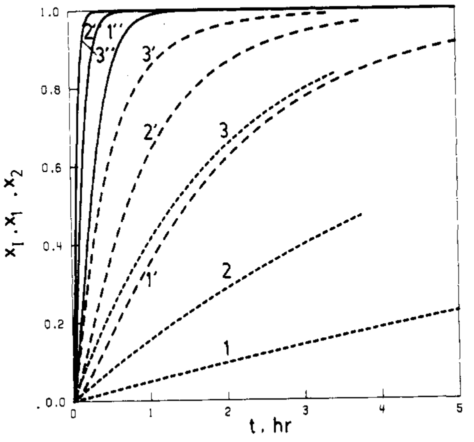

**Figure 9.** Effect of the reaction temperature, $T$, on the conversion of the initiator, $x_I$ (curves 1, 2, and 3), styrene, $x_1$ (curves 1', 2', and 3'), and *p*-DVB, $x_2$ (curves 1'', 2'', and 3'') during the reaction of styrene and *p*-DVB using a cross-linking ratio of $X = 0.010$ and an initiator concentration of $I_0 = 0.1$ mol/L. Three different temperatures were used: $T = 75$ °C (curves 1, 1', and 1''), $T = 85$ °C (curves 2, 2', and 2''), and $T = 95$ °C (curves 3, 3', and 3'').

conversions increase as shown in Figure 8. The polymerization ceases early for high values of the initial concentration of the initiator due to vitrification, because of the high monomer conversions.

The temperature dependence of the kinetic constants is responsible for the high propagation rates at elevated temperatures. Therefore, the monomers are consumed faster at high temperatures as shown in Figure 9 for the copolymerization/cross-linking reaction of styrene with *p*-DVB. The variation of $\bar{M}_n$ depends on the relative change of the reaction rates. The higher the temperature, the lower the average molecular weight of linear polymer as shown in Figure 10.

As previously discussed, there is an inversion in the effect of temperature on the average number of effective cross-links, because of the increased polymer concentration at high temperatures. Eventually the value of $\nu_e$ decreases as the temperatures ranges from 75 to 95 °C. For the reaction of styrene with *p*-DVB or *m*-DVB high temperatures result in fast cessation of the polymerization, because of the high monomer conversions.

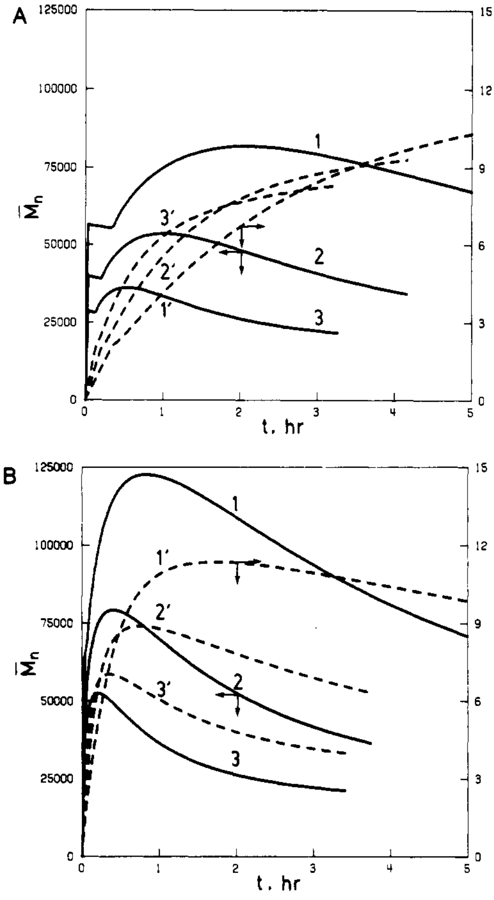

**Figure 10.** Effect of the reaction temperature, $T$, on the number-average molecular weight, $\bar{M}_n$ (curves 1, 2, and 3), and the average number of effective cross-links per chain, $\nu_e$ (curves 1', and 2', and 3'), during the reaction of styrene with (A) *m*-DVB using a cross-linking ratio of $X = 0.050$ and (B) *p*-DVB using a cross-linking ratio of $X = 0.010$. The initiator concentration, $I_0$, was 0.1 mol/L. Three different temperatures were used: $T = 75$ °C (curves 1 and 1'), $T = 85$ °C (curves 2 and 2'), and $T = 95$ °C (curves 3 and 3').

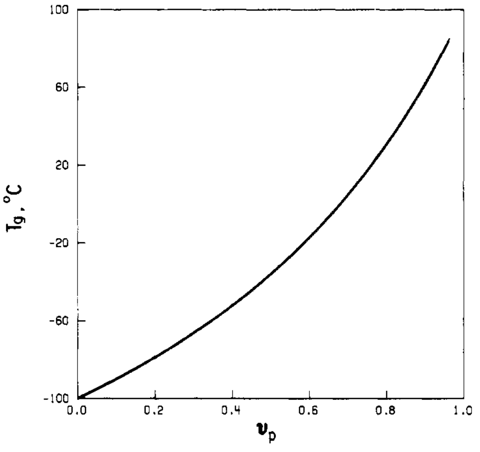

**Figure 11.** Dependence of the glass transition temperature on the polymer volume fraction in the monomer-swollen polymer during the styrene/*p*-DVB copolymerization/cross-linking reaction at 85 °C using a cross-linking ratio of $X = 0.010$ and an initiator concentration of $I_0 = 0.1$ mol/L.

The polymerization reaction ceases due to vitrification when the reaction temperature becomes equal to the glass transition temperature of the polymer system. The glass transition temperature is calculated by using eq 31. The dependence of the glass transition temperature on the polymer volume fraction is shown in Figure 11 during the copolymerization/cross-linking reaction of styrene with *p*-DVB at 85 °C, for $X = 0.010$ and $I_0 = 0.1$ mol/L. The glass transition temperature of the polymer is constant up

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to the gel point. Afterward, it is related to the mole fraction of cross-linked monomer units through eq 35.

**Registry No.** *p*-DVB, 105-06-6; *m*-DVB, 108-57-6; styrene, 100-42-5; (styrene)·(*p*-DVB) (copolymer), 25086-67-3; (styrene)·(*m*-DVB) (copolymer), 25703-32-6.

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# Intramolecular Dimer Radical Cations of $\alpha,\omega$-Di(2-naphthyl)alkanes and Poly(2-vinylnaphthalene)

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ABSTRACT: Dimer radical cation formation in $\alpha,\omega$-di(2-naphthyl)alkanes [(2-naphthyl)–$(CH_2)_n$–(2-naphthyl), ($n$ = 3, 6, 12)] and poly(2-vinylnaphthalene) was measured by the pulse radiolysis method. Two kinds of intramolecular dimer radical cations at 580 and 660 nm were observed for 1,3-di(2-naphthyl)propane and poly(2-vinylnaphthalene), whereas only one dimer radical cation absorption was detected at 580 nm for 1,12-di(2-naphthyl)dodecane. The dimer radical cation with $\lambda_{max}$ at 580 nm converted to another form with $\lambda_{max}$ at 660 nm in 20 ns for 1,3-di(2-naphthyl)propane and in 70 and 125 ns for the polymer with the molecular weight of 1950 and $1.2 \times 10^5$, respectively. The activation energies of the conversion, 7.4 ± 1.0 and 9.0 ± 1.0 kcal/mol, were obtained for the 1,3-di(2-naphthyl)propane and the polymer (MW = $3.8 \times 10^4$), respectively. The conversion process is interpreted as follows. Two kinds of dimer radical cations with different geometrical structures, partial and fully overlapped sandwich structures, are produced through a kinetically controlled process involving the interaction of the monomer radical cation with the ground-state chromophore of the same molecule. Then the unstable partially overlapped state slowly converts in approximately 100 ns to a thermodynamically more stable form, the fully overlapped state, via the double rotation of the chains, unfolding of the chain to the open form, and refolding to the sandwich structure. Solvent effects on the conformational change in the polymer system are also examined.

## Introduction

Since the pioneering work of intramolecular excimer formation in diphenylalkanes was carried out by Hirayama,[1] these bichromophoric compounds are recognized as favorable systems for studying the geometrical aspects of the excimer state as well as the dynamics of the conformational changes of vinyl polymer chains.[2-23] Bovey et al.[2] first pointed out the importance of configurational considerations in excimer-forming capacity by using diastereoisomeric 2,4-diphenylpentanes. The difference in the excimer intensity between meso and racemic isomers can be explained by the NMR results concerning the conformational distribution within each isomer in the ground state.

The understanding of the geometrical structures of excimer conformations in bichromophoric systems has been much advanced by the extensive study of De Schryver et al.[4-8] on the transient behavior of the excited state of 2,4-diarylpentanes and 1,1-diaryldiethyl ethers. Two excimers with different geometrical structures have been observed most clearly in meso and racemic 2,4-di(*N*-carbazoyl)pentanes and are related to the two excimers observed in poly(*N*-vinylcarbazole).[9,11,14] The geometrical arguments concerning excimer conformation have been recently extended to the conformation of dimer radical cations in bichromophoric systems and polymers.[10,24]

In a previous paper, we have shown that radical cations of phenyl and naphthyl chromophores in bichromophoric systems and polymer systems have an intramolecular interaction with ground-state chromophores even in a rigid glass matrix at 77 K and have shown that the absorption spectrum varies remarkably with changes in intermolecular distances.[25] The dimer radical cation is a sensitive probe for evaluating weak and rather long distance inter- and intramolecular interactions in comparison with the excimers.[10,25] In addition, because of its long lifetime, the probe gives us information concerning slow conformational changes in polymer chains.

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