Intramolecular Crosslinking in Gelation

Hiroo Iwata and Yoshito Ikada*

Acetalization of poly(vinyl alcohol) (PVA) carrying mostly two terminal aldehyde groups was studied in aqueous acidic solution at different PVA concentrations. The transition from sol to gel or *vice versa* took place at the temperature, where an equilibrium was reached between acetalization and deacetalization. Using known rate constants for intra- and intermolecular acetalization as well as that for deacetalization, we could evaluate the extent of reaction at the sol-gel transition temperature, *i.e.*, at the gel point. Comparison of the observed with the theoretical extent of reaction at the gel point revealed that contribution of intramolecular acetalization to the overall reaction was too large to be neglected. It was concluded that two types of intramolecular crosslinkings, both ineffective for gelation, were operative, the one producing a small ring and the other a large ring.

KEY WORDS: Poly(vinyl alcohol) / Terminal aldehyde groups / Inter- and intramolecular acetalization / Sol-gel transition temperature / Gel point /

INTRODUCTION

Since Flory's pioneering work[1], several authors have presented theories on gelation which results from polymerizations in the presence of multifunctional monomers as well as crosslinking of prepolymers.[2-4] However, only few works[5] have been devoted to compare the gelation theories with experiments because of difficulty in determining the extent of the reaction, in particular near the so-called gel point at which macromolecules with an infinite weight-average molecular weight are to be formed. This point is easily observable, especially if the reaction system has a low viscosity prior to the reaction, since it sets to a gel devoid of fluidity at the gel point.

We have undertaken to study gelation of poly(vinyl alcohol) (PVA) having aldehyde groups at both chain-ends in aqueous acidic solution. As acetalization proceeds between hydroxyl and aldehyde groups in different PVA molecules, the solution gradually becomes viscous, finally setting to a gel. Recently we have revealed that aldehyde groups are generated at ends of PVA molecules upon oxidation with ceric ions in aqueous HNO_3 medium at low temperatures.[6] Indeed, the terminal aldehyde groups underwent acetalization with hydroxyl groups of PVA, leading to gelation. In another paper, kinetic studies were carried out on the inter- and intramolecular acetalization of PVA carrying terminal aldehyde groups in an attempt to assess the effect of long-range interaction on the polymer-polymer reaction rate.[7] A theory on the excluded volume effect on polymer-polymer reactions will be described elsewhere.[8]

The present study is aimed to determine the extent of reaction at the gel point

* 岩田博夫, 筏 義人: Laboratory of Fiber Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

and to compare the result with a theoretical prediction in order to estimate the crosslinks ineffective for gelation.

<div align="center">EXPERIMENTAL</div>

Preparation of PVA Carrying Terminal Aldehyde Groups

Vinyl acetate(VAc) was subjected to simple distillation and then fractionally distilled after polymerization up to a *ca.* 15 % conversion by addition of 2, 2'-azobisisobutyronitrile. A middle fraction of the distillate giving a boiling point of 72–73°C was used for the subsequent radiation polymerization. It was conducted with gamma rays from a Co-60 source after degassing the monomer with a freeze-thaw method, followed by sealing. The temperature and the dose rate employed for the polymerization are tabulated in Table I, together with $\bar{P}_n$ and the content of 1, 2-glycol units in PVA obtained on complete hydrolysis of the PVAc formed. The PVA materials were subjected to oxidation with sodium periodate to cleave selectively the 1, 2-glycol units present in PVA under formation of aldehyde groups at both chain-ends of the degraded PVA. The oxidation was carried out in aqueous PVA solution of 5 g·dl^{-1} at room temperature for 1 hr. Determination of the concentration of periodate consumed by the oxidation permits us to calculate the number of terminal aldehydes per oxidized PVA molecule, which is given in Table II, together with $\bar{P}_n$ of the oxidized PVA. The table also includes the result of oxidation for a commercial PVA with $\bar{P}_n$ of 1340 and a 1, 2-glycol content of 1.8 mol%. Values of λ, μ, and α_g given in Table II will be discussed later.

<div align="center">Table I. Characteristics of PVAc Obtained by Radiation Polymerization</div>

	Polym. Temp. °C	Dose rate rad. sec^{-1}	$\bar{P}_n$	1,2-glycol unit mol %
PVAc-1	0	4.94	4,750	1.20
PVAc-2	−78	13.9	811	0.65

<div align="center">Table II. Characteristics of Periodate-Oxidized PVA</div>

Starting PVAc	Oxidized PVA	$\bar{P}_n$	Number of aldehyde groups per molecule	λ	μ	α_g
PVA-C[a]	PVA-0	53	1.92	0.08	0.92	0.260
PVAc-1	PVA-1	513	1.80	0.20	0.80	0.279
PVAc-2	PVA-2	176	1.57	0.43	0.57	0.325

a) a commercial PVA with $\bar{P}_n$ of 1,340 and a 1,2-glycol content of 1.8 mole %.
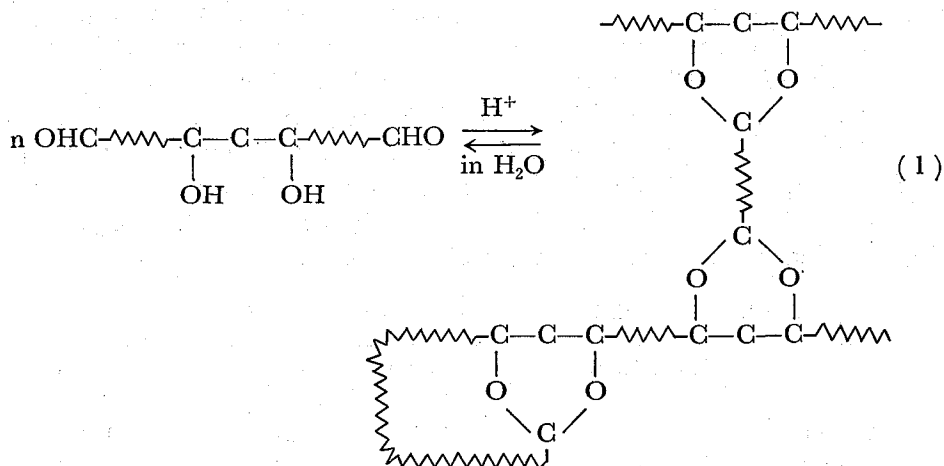
Acetalization

As the gel point we determined the critical temperature at which reversible sol-gel transition of reaction mixtures took place. For this purpose, acetalization of PVA in aqueous solutions of different polymer concentrations was allowed to proceed at room temperature in the presence of 0.5 N HCl as a catalyst till formation of a gel. Then temperature was raised to the point at which the gel was trans-

formed into a sol as a result of shift of the equilibrium between acetalization and deacetalization. The sol-gel transition was reversible and the temperature could be readily determined with visual inspection. In the case of determination of variation in the extent of acetalization with time, the reaction was performed at 50°C in the presence of 0.05 N HCl at a polymer concentration of 4.88 g·dl^{-1}. At regular time intervals, the aliquot of reaction mixture was pipetted out and neutralized with aqueous NaOH solution to prevent the further reaction. The concentration of aldehyde groups remaining unreacted was determined by colorimetry with 3-methyl-2-benzothiazolone hydrazone hydrochloride(MBH).[9]

RESULTS

Acetalization is a reversible reaction in which the rates of forward and backward reactions become considerably high under a suitable condition. In the case of PVA with terminal aldehydes acetalization may proceed as follows:

$$n \; OHC\text{-}\mathcal{W}\text{-}\underset{OH}{\overset{}{C}}\text{-}C\text{-}\underset{OH}{\overset{}{C}}\text{-}\mathcal{W}\text{-}CHO \xrightleftharpoons[\text{in } H_2O]{H^+} \qquad\qquad (1)$$

A clear transition between sol and gel takes place promptly in a reversible manner on a slight change in temperature. Figure 1 illustrates an example of a plot of the
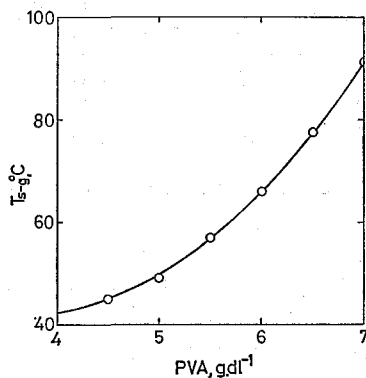

Fig. 1. Dependence of sol-gel transition temperature, T_{s-g}, on polymer concentration (PVA-0, 0.5 N HCl).

sol-gel transition temperature as a function of concentration of PVA solutions. The polymer employed is PVA-0.

The critical extent of reaction of terminal aldehydes at the gel point can be estimated on the basis of theory derived by Saito,[10] if it is assumed that only inter-molecular crosslinking occurs. When the reaction mixture contains three kinds of polymers, i.e., a polymer without terminal functional group, a polymer with one terminal functional group, and a polymer with two terminal functional groups, the theory predicts that the distribution function $m_i(p, \tau)$ of degree of polymerization p is to satisfy the following differential equation.

$$\frac{\partial m_i(p, \tau)}{\partial \tau} = -\{p f_{01}(\tau) + i f_{10}(\tau)\} m_i(p, \tau)$$
$$+ \sum_{j=0}^{i} (i-j+1) \int_0^p l m_j(l, \tau) m_{i-j+1}(p-l, \tau) \mathrm{d}l \tag{2}$$

Here, i, j, and $i-j+1$ mean the numbers of terminal reactive groups in starting and resultant macromolecules. τ is related to the extent of reaction α by the equation

$$\alpha = 1 - e^{-\tau} \tag{3}$$

$f_{01}(\tau)$ and $f_{10}(\tau)$ are defined as

$$f_{st}(\tau) = \sum_{i=0}^{\infty} i^t \int_0^{\infty} p^s m_i(p, \tau) \mathrm{d}p \tag{4}$$

Provided that our prepolymers have initially a random molecular weight distribution, irrespective of the number of aldehydes attached, the solution of Eq.(2) leads to the conclusion that $\bar{P}_n$ and $\bar{P}_w$ to be observed at α are equal to

$$\bar{P}_n(\alpha) = \frac{\bar{P}_n(0)}{1 - \alpha \mu (1 + \lambda)} \tag{5}$$

$$\bar{P}_w(\alpha) = \frac{C_1 C_2}{C_2^2 \{\sqrt{\widetilde{C_1}} + C_3(1-\alpha)\}^2 - (1-\alpha)^2} \tag{6}$$

with

$$C_1 = \frac{\bar{P}_n(0)}{\mu}, \quad C_2 = \frac{(\lambda + 2\mu - 1)^2}{2\bar{P}_n(0)} - \frac{2\mu}{\bar{P}_n(0)}$$
$$C_3 = -\frac{1}{C_2} \sqrt{1 + \frac{C_2 \bar{P}_n(0)}{2\mu}} - \sqrt{C_1} \tag{7}$$

where λ and μ are the fractions of prepolymer molecules having one and two terminal aldehyde groups, respectively. These values are given in Table II. Figure 2 shows $\bar{P}_n(\alpha)$ and $\bar{P}_w(\alpha)$ calculated with the use of Eqs.(5) and (6) for PVA-1.

Since $\bar{P}_w$ should become infinite at the gel point, inserting $1/\bar{P}_w = 0$ into Eq.(6) leads to

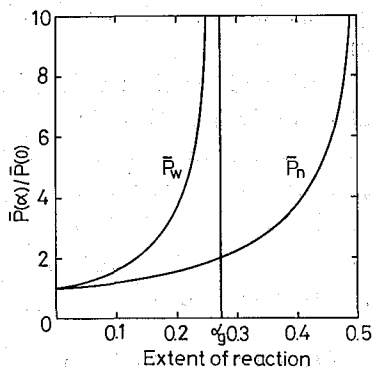$$\alpha_g = 1 + \frac{C_2 \sqrt{C_1}}{1 + C_2 C_3} \tag{8}$$

Fig. 2. Variation of $\bar{P}_w(\alpha)/\bar{P}_w(0)$ and $\bar{P}_n(\alpha)/\bar{P}_n(0)$ as a function of extent of reaction α, when the crosslinking is exclusively due to intermolecular reaction (PVA-1).

where α_g is the extent of reaction at the gel point and was given in the last column of Table II.

On the other hand, the extent of reaction can be directly determined from reduction in the aldehyde concentration during reaction. Figure 3 demonstrates the result of acetalization for PVA-0 carried out at 50°C for a polymer concentration of 4.88 g·dl⁻¹. Contrary to the theoretical prediction, gelation did not occur even when the reaction proceeded to extents significantly higher than 0.261, *i.e.*, the theoretical α_g of this PVA. Under this reaction condition, the mixture reached an equilibrium without setting to a gel. However, lowering temperature brought about gelation expectedly, but in this case it was very difficult to follow the change of the aldehyde concentration with the MBH method. Thus an alternative method
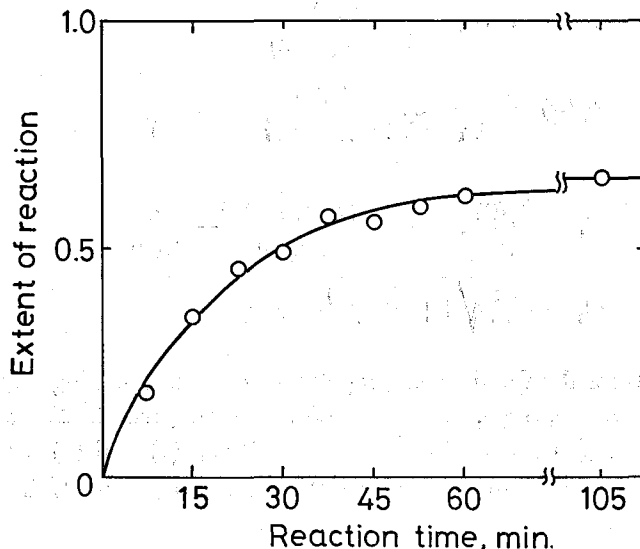

Fig. 3. A plot of extent of acetalization against time (PVA-0, [OH]₀ =1.11 mol·1⁻¹, 50°C, 0.05 N NCl).

was followed to measure the true extent of reaction at the gel point, α_t. The method we applied will be described in the following.

The rate of acetalization is in our case given by

$$-\frac{d[CHO]}{dt} = k_1[CHO] + k_2[OH]_0[CHO] - k_{-2}[acetal][H_2O]_0 \qquad (9)$$

Here the concentrations of hydroxyl groups and water are assumed to remain constant and to be equal to the initial concentrations, $[OH]_0$ and $[H_2O]_0$, resp., because the

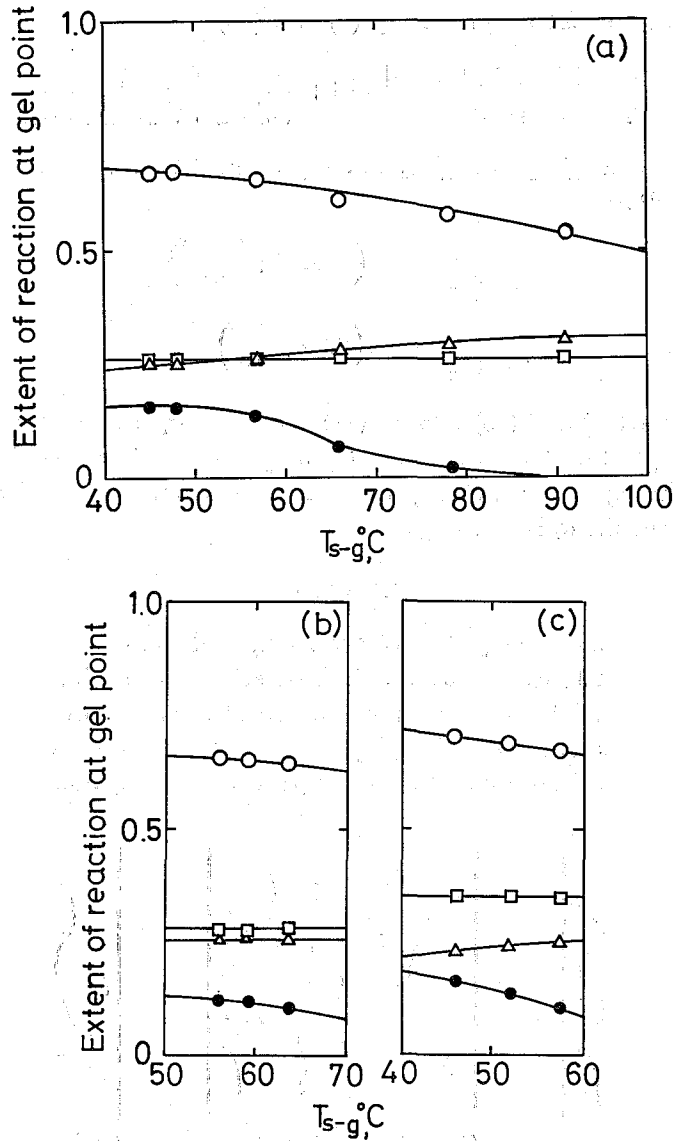Fig. 4. Extents of each reaction at gel point for different PVA materials ((a) PVA-0; (b) PVA-1; (c) PVA-2).
○ α_t (true); □ α_g (INTER); △ $\alpha_{INTRA-I}$ (INTRA-I);
● $\alpha_{INTRA-II}$ (INTRA-II)

concentrations of aldehyde, [CHO], and acetal formed, [acetal], are extremely low as compared with $[OH]_0$ and $[H_2O]_0$. k_2 and k_{-2} are the rate constants of acetalization and deacetalization, resp., while k_1 is the first-order rate constant for intramolecular acetalization in the same prepolymer. As an equilibrium is reached at the sol-gel transition temperature with

$$-\frac{d[CHO]}{dt} = 0 \qquad (10)$$

the α_t value can be obtained from Eqs.(9) and (10).

$$\frac{1}{\alpha_t} = \frac{[acetal]+[CHO]}{[acetal]} = 1 + \frac{[H_2O]_0}{(k_1/k_{-2})+(k_2/k_{-2})\,[OH]_0} \qquad (11)$$

The dependence of k_1/k_{-2} and k_2/k_{-2} on temperature, T, has been determined in the previous paper[7] as

$$\frac{k_2}{k_{-2}} = \exp\left(-7.05+\frac{3,570}{T}\right) \qquad (12)$$

$$\frac{k_1}{k_{-2}} = \exp\left(2.29+\frac{450}{T}\right) \qquad (13)$$

By inserting Eqs.(12) and (13) into Eq.(11), we obtain α_t as a function of the sol-gel transition temperature that is identical to the gel point. The calculated values of α_t are given in Fig. 4. It is clearly seen that discrepancy between the theoretically estimated α_g and the α_t is very large.

DISCUSSION

The terminal aldehyde groups of PVA may undergo either intermolecular or intramolecular acetalization reaction. This is schematically illustrated in Fig. 5. It is likely that the intramolecular acetalization of aldehyde involves two types of reaction; the one is with the hydroxyl groups belonging to the same prepolymer as the aldehyde, while the other reaction takes place with the hydroxyl groups of other

(a) Intermolecular
reaction(INTER)

(b) Intramolecular
reaction(INTRA-I)
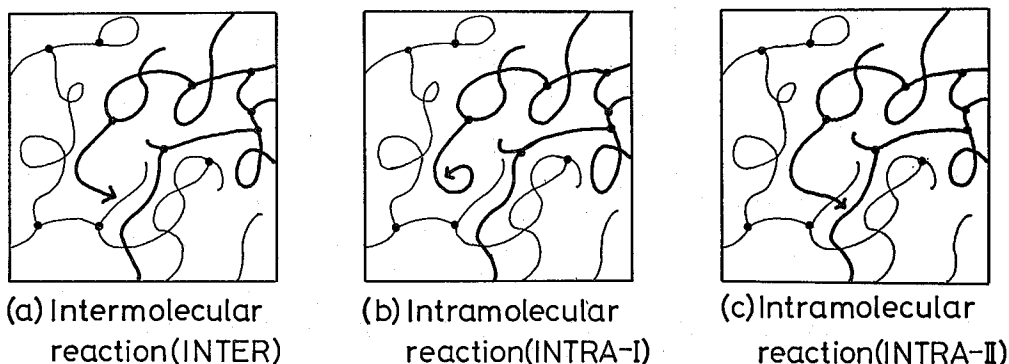
(c) Intramolecular
reaction(INTRA-II)

Fig. 5. Schematic representation of inter- and intramolecular reactions.

prepolymers that are linked directly or indirectly to its own prepolymer. Both the intramolecular reactions lead to ineffective crosslinks, in contrast to the intermolecular acetalization. Let us designate the former ineffective acetalization INTRA-I, the latter INTRA-II and the effective intermolecular acetalization INTER. In the following we will formulate the contribution of these reactions.

In Eq. (9), the first term represents the rate of acetalization in infinitely dilute solution, that is, acetalization between the terminal aldehyde and the hydroxyl groups belonging to the same prepolymer. Thus the first term can be rewritten as

$$k_1[CHO] = k_2[OH]_{INTRA-I}[CHO] \tag{14}$$

or

$$\frac{k_1}{k_2} = [OH]_{INTRA-I} \tag{15}$$

where $[OH]_{INTRA-I}$ is the concentration of hydroxyl groups effective for the intramolecular reaction, INTRA-I.

As is evident from Eqs. (9), (14), and (15), the contribution of INTRA-I to the overall extent of acetalization at gel point is given by

$$\alpha_{INTRA-I} = \alpha_t \times \frac{[OH]_{INTRA-I}}{[OH]_0 + [OH]_{INTRA-I}} \tag{16}$$

From this equation $\alpha_{INTRA-I}$ can be evaluated with use of the following kinetic relation found in the previous work[7]

$$[OH]_{INTRA-I} = \frac{k_1}{k_2} = \exp\left(9.34 - \frac{3,120}{T}\right) \quad \text{(unit: mol·l}^{-1}) \tag{17}$$

and is plotted in Fig. 4 against temperature for PVA-0, PVA-1, and PVA-2. As is clearly seen, $\alpha_{INTRA-I}$ is as large as α_g, that is, the extent of intermolecular acetalization. The main reason for the large $\alpha_{INTRA-I}$ is because the reaction is occurring in dilute solutions. It should be further emphasized that the sum of α_g and $\alpha_{INTRA-I}$ is significantly lower than α_t, at least in the temperature range below about 70°C. This strongly suggests that INTRA-II acetalization cannot be ignored.

In contrast to the INTRA-I acetalization, whose rate is not dependent of $[OH]_0$, the INTRA-II acetalization is not so simple. Near the gel point, any of the aldehyde groups remaining unreacted in the resultant branched polymer will undergo acetalization with the hydroxyl groups of its own prepolymer ($[OH]_{INTRA-I}$), with those of the other prepolymers constituting the branched polymer ($[OH]_{INTRA-II}$), or with those of any other polymers ($[OH]_0 - [OH]_{INTRA-II}$). Therefore the hydroxyl concentration in the vicinity of this aldehyde group may be equal to

$$[OH]_{INTRA-I} + [OH]_{INTRA-II} + ([OH]_0 - [OH]_{INTRA-II})$$

The last term refers to the hydroxyl groups which lead to intermolecular crosslinking, INTER. Acetalization with other hydroxyl groups than this $[OH]_{INTER}$ results in formation of ineffective crosslinks.

The $[OH]_{INTRA-II}$ cannot be determined experimentally, in contrast to $[OH]_{INTRA-I}$.[7] Its theoretical evaluation is also very difficult. Thus the $\alpha_{INTRA-II}$ given in Fig. 4 was obtained by substracting $\alpha_g + \alpha_{INTRA-I}$ from α_t.

The reason for the predominant temperature dependence of $\alpha_{INTRA-II}$ is not clear to us, but it seems likely that this may be partly originated from poor accuracy of k_1/k_2 ratios at high temperatures, because they were determined by extrapolating the k_1/k_2 ratios found in the narrow temperature range from 30°C to 55°C under the assumption of linearity of Arrhenius plots. On the other hand, Saito concluded from his statistical theory that intramolecular reaction would be ignored. In his treatment the intramolecular reactive groups are assumed to be distributed homogeneously all over the reaction system. However, it is impossible for the reactive groups responsible to INTRA-I to exist far away from this terminal group because of attaching to the same prepolymer as the terminal group. In addition, the reactive groups of INTRA-II seem not to be diffusable throughout in the reaction system in a short time, especially near the gel point where the viscosity of the reaction system is very high. The discrepancy between our experimental results and his theoretical prediction may be attributed to inapplicability of his assumption to our experimental condition.

In conclusion, we may state that the disagreement of the true extent of reaction α_t with the theoretically estimated extent α_g at the gel point will be attributed to occurrence of two types of intramolecular reactions. One of them is the reaction INTRA-I producing small rings in the vicinity of the end of polymer chain. The other is the reaction INTRA-II producing large rings in the polymer network. In any of gelation theories attempting to assess the extent of reaction at the gel point, both of these intramolecular reactions should be taken into account, in particular for the reaction in solution, although they do not participate in the network formation.

REFERENCES

(1) P.J. Flory, *J. Amer. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941).
(2) W.H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).
(3) A. Charlesby,: Atomic Radiation and Polymers", 1960, Pergamon Press, New York.
(4) O. Saito, in "The Radiation Chemistry of Macromolecules", Vol. I, M. Dole, Ed., 1972, Academic Press, New York.
(5) P.J. Flory, "Principles of Polymer Chemistry, 1953, Cornell Univ. Press, Ithaca, New York.
(6) Y. Ikada, Y. Nishizaki, H. Iwata, and I. Sakurada, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 451 (1977).
(7) H. Iwata and Y. Ikada , *Macromolecules*, **12**, 287 (1979).
(8) H. Iwata and Y. Ikada, *Makromol. Chem.*, in press.
(9) E. Sawicki, T.R. Hanser, T.W. Stanley, and W. Elbert, *Anal. Chem.*, **33**, 93 (1961).
(10) O. Saito, *Polymer Engineering and Science*, **19**, 234 (1979).