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Interpretation of Gel Points of an Epoxy-Amine System Including Ring Formation and Unequal Reactivity: Measurements of Gel Points and Analyses on Ring Structures.

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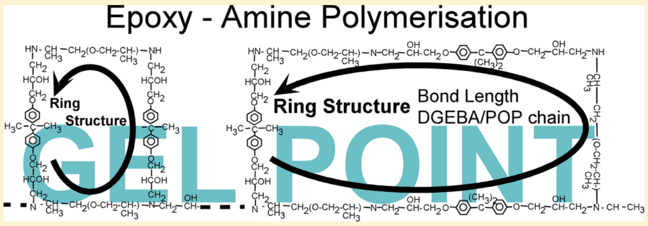

ABSTRACT: Gel points are investigated as the critical extent of reaction at gelation by FT-IR and viscoelastic measurements for the network formed by the epoxy−amine system. The reaction systems examined are comprised of diglycidyl ether of bisphenol A (DGEBA) and polyoxypropylene (POP) diamine of different chain lengths with various degrees of dilution. The experimental results are obtained as the delay of gel point, that is the delay from the gel point expressed by the Flory−Stockmayer formula, and interpreted in terms of ring formation caused by intramolecular reaction which is characterized by the ring forming parameter of λ_0. This parameter relates with the internal concentration (in mol L^{-1}) of reactive groups P_{ab}, for $RA_{fa} + R'B_{fb}$ type polymerization. The analyses of the conversion curve (p vs t curve, where p denotes the extent of reaction) obtained by FT-IR measurement are carried out on the basis of the kinetic model of the epoxy-amine reaction to find the ratio of rate constant. For all the reaction systems, gelation occurs in excess of Flory−Stockmayer gel point; the excesses are 0.09−0.15 in extent of reaction. λ_0 is determined from the gel point data through the p_c−λ_0 relationship developed in the first part of this study, where the schemes of unequal reactivity and the states of reaction for POP diamine unit are incorporated. The gel point data are also applied to the p_c−λ_0 relationship where these schemes are not incorporated. Following λ_0, P_{ab} and the length of bond are derived and compared in terms of the effect of difference in these schemes.

1. INTRODUCTION

The rheological behavior of sol − gel transition of chemical and physical gels has been studied theoretically and experimentally. As shown in these studies, topological concepts, often using a fractal approach, is important in discussing rheological properties of gel. Ring structure takes one of significant factors in grasping polymer networks topologically.[1,2] Further, one of the important properties closely related to ring structure is the delay of gel point.[3−5] The gel point observed experimentally delays from Flory −Stockmayer gel point because of the intramolecular reaction in the course of network formation, which is generally given by $RA_{fa} + R'B_{fb}$ type polymerization.[6] More precisely, in addition to rings other molecular structures, such as dangling chains, can delay the gel point. Therefore, identification for all the factors within the network is required in order to understand the properties of gel in connection with the network structure completely. In particular, the relationship between the delay of gel point and ring structure has been attractive to many research groups.[7,8]

In the first part of this study, a theoretical method was shown to relate the gel point to ring-forming parameter, λ_0, for the gelation of an epoxy − amine system based on diglycidyl ether of bisphenol A(DGEBA) and polyoxypropylene (POP) diamine, that is, the polymerization of $RA_4 + RB'_2$.[9,10] The method incorporates detail of molecular structures as well as the features of the unequal reactivity between the hydrogen atoms of the primary and the secondary amine groups, which is an extension of our previous work of the Ahmed−Rolfes−Stepto (ARS) theory.[2] This is to predict the gel point directly from network formation and reactant structure accounting for intramolecular reaction.

Because it has been shown that the accurate, direct Monte Carlo modeling of gel point is very difficult for finite populations of reactive groups, ARS theory was proposed as the best approach that accounts for the ring structures reasonably and can be applied to a wide range of polymerization.[11,12] In its most general form, ARS theory approaches polymerizations of reactants bearing A groups and B groups of functionalities of f_a and f_b. For such polymerizations, the theory evaluates the probability of chain growth between statistically equivalent points of randomly chosen two reactive groups. Consequently, ring structures of all sizes are accounted for. The ring-forming parameter characterizes the competition between intermolecular and intramolecular reaction, and relates with the internal concentration, P_{ab}. P_{ab} is the mutual internal concentration (in

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mol L^{-1}) of an A and B group on the same molecule which can react to form the smallest ring structure.

$$P_{ab} = \frac{1}{N_{AV}}\left(\frac{3}{2\pi\langle r^2\rangle}\right)^{3/2} \tag{1}$$

The A group is the H atom of the amine group and B is the epoxy group. $\langle r^2\rangle$ is the mean-square end-to-end distance of the linear subchain joining two groups which can be about to react intramolecularly. It has a relationship with ν_s and b, where ν_s is the number of bonds and b, the bond length of the subchain.

$$\langle r^2\rangle = \nu_s b^2 \tag{2}$$

Epoxy resins comprise a group of cross-linkable material; their chemistry and technology have been reported in a number of literatures.[13−15] In particular, Dušek and co-workers have published many articles and reviews through decades concerning epoxy resins.[16] Those papers are concerned with rate constants,[17] cure with different kinds of amines,[18] inhomogeneous growth of cross-linking.[19] The delay of gel point for cross-linking of diepoxides with diamines has also discussed experimentally and theoretically with branching processes.[20,21] As described in the literature, the epoxy resin is of interest from an industrial point of view and broadly used with valuable properties. In addition, it has also been taken as a research object to discuss the relation between network structure and rheological properties, in particular, the critical phenomena of viscosity and elasticity.[22−25] However, research works to consider the ring-formation for the epoxy network are limited. This study shows the measurement of gel point using chemo-rheological method and determination of P_{ab}, b characterizing the ring structure. In addition, the values of P_{ab}, b derived are compared with the results of the previous work, in which the detail of molecular structures or the features of the unequal reactivity were not incorporated.

2. EXPERIMENTAL SECTION

Materials. Diglycidyl ether of bisphenol A (DGEBA) was kindly supplied by Dow Chemical Nippon. Product name: D.E.R.332, Lot: QK0601M101. Average repeating number: n_{BA} = 0.03, Molecular weight: M_n = 349. Polyoxypropylene (POP) diamine was purchased from Aldrich Chemical Co. Average value of M_n for POP diamines are 230, 400, and 2000; they are called D230, D400, and D2000, respectively. The ratio of activation for the amine group is 98% on average according to the supplier data. Tetraethylene glycol dimethyl ether (Tetraglyme) was purchased from Kanto Chemical Co., Inc. These chemicals were used without further purification.

The polymerization solution was diluted with Tetraglyme. The use of different dilutions of reactants leads to different amounts of intramolecular reactions, different gel points and different network structures. All the polymerization solution was prepared in the reactive group ratio of r = 1 assuming that the functionality distribution for POP diamine used in this work is negligible; r is defined as, $r = (c^0_{H1}/c^0_{EP})$, where c^0_{H1} and c^0_{EP} are concentrations of H atom in amine group of POP diamine and epoxy group before the reaction starts, respectively. Degree of dilution is shown by D, the weight fraction of Tetraglyme; $D = 100 \times w_{Tetraglyme}/(w_{DGEBA} + w_{POP\ diamine} + w_{Tetraglyme})$.

Methods. Dynamic viscoelasticity of the polymerization solution was measured to determine gelation time using ARES 100FRT-(Rheometric Scientific F. E. Ltd.) with disposable parallel cells of $\phi = 40$. Multiwave method was used to obtain G', G'' data in every 0.5 min in the frequency range from ca. 0.8 to 100 rad/s. It is demonstrated that this technique effectively decouples the frequency dependence and time dependence of the fluid properties.[26] This enables us to directly obtain the complex moduli of G' and G'', at several frequencies simultaneously as the system structure evolves with time. As for the choice of the strain within the linear viscoelastic regime, the measurements were repeated using several strain amplitudes in the range from 0.1 to 40% to carry out suitably.

FT-IR measurement was performed using MAGNA(Nicolet Inc.). The absorption peak of the epoxy group (4530 cm^{-1}) was used to measure the extent of reaction, p, with reference to the absorption of phenyl group (4620 cm^{-1}) which is contained in DGEBA[27]

$$p = \frac{A_0 - A_t}{A_0} \tag{3}$$

where A_0 is the absorbance of the glycidyle group before reaction, and A_t is that at given time.

The glass transition temperature (T_g) of the polymer of DGEBA and POP diamine was investigated by DSC so as to carry out both viscoelasticity and FT-IR measurement above T_g. In general, T_g of the polymer of DGEBA and POP diamine is a function of degree of cure.[28] Therefore, several samples were prepared with different reaction times using a constant reaction temperature of 90 °C. $T_{g\infty}$, the glass transition temperature of a fully cured sample was determined as $T_{g\infty} \approx 83$ °C for the polymer of DGEBA and D230. All the measurements of FT-IR and rheology were performed at 90 °C .

In the sample preparation, DGEBA, POP diamine, and Tetraglyme were first weighed and mixed at room temperature, then poured into either IR cell or rheometer cell preheated at 90 °C. It was checked by FT-IR spectroscopy in advance that the reaction at room temperature is negligible. From the measurements of FT-IR and rheology, the critical extents of reaction at gelation, p_c were determined.

3. RESULTS

Figure 1 shows plots of absorbance vs wavenumber for the polymerization of DGEBA and D230 of D = 0 at different reaction times, t, in the range 4450−4700 cm^{-1}. After the measurement in 90 °C, it was heated to 160 °C and left for post cure until the spectrum no longer changed. Then temperature was lowered to 90 °C again and a spectrum was acquired, which was denoted as after post cure.

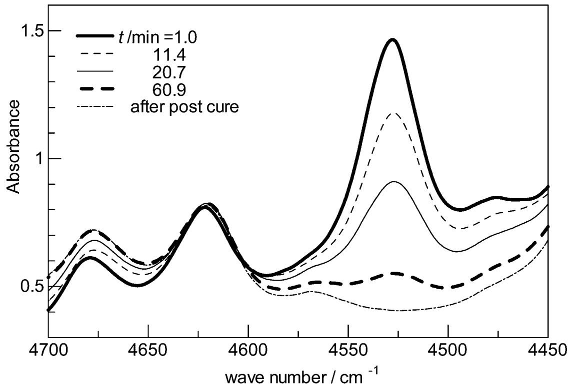

Figure 1. FT-IR spectra for the polymerization system of DGEBA and D230(D = 0) at 90 °C, recorded after heating for 1, 11.4, 20.7, and 60.9 min and after post cure.

As can be seen in Figure 1, the absorbance at 4530 cm^{-1} decreased with increasing the reaction time, which is ascribed to a decrease in the number of epoxy group. On the other hand, the absorbance at 4620 cm^{-1} remained constant during reaction, which is ascribed to a constant concentration of phenyl group in DGEBA. Plots of p for polymerization systems of D230 and D2000 as functions of reaction times are shown in Figures 2 and 3 for systems of various degree of dilution, respectively. It can be seen that the reaction rate becomes slower as the increase in the

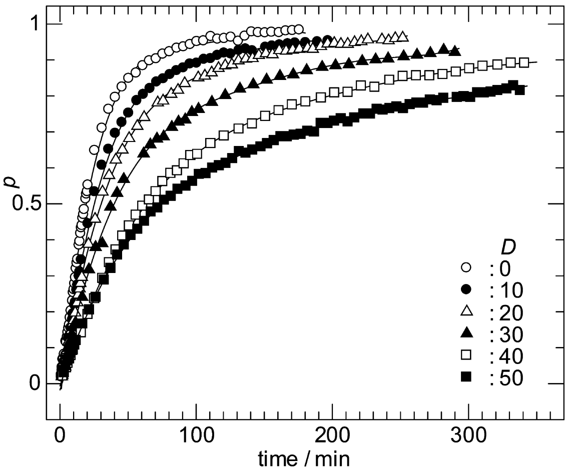

Figure 2. Conversion versus time profiles for polymerization systems of DGEBA and D230 with different dilutions *D*. Temperatures employed are 90 °C.

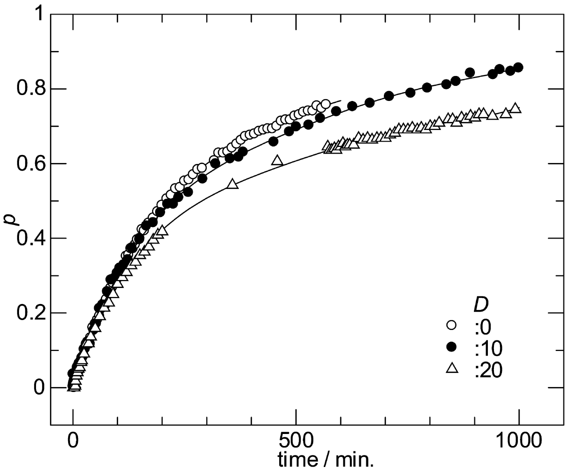

Figure 3. Conversion versus time profiles for polymerization systems of DGEBA and D2000 with different dilutions *D*. Temperatures employed are 90 °C.

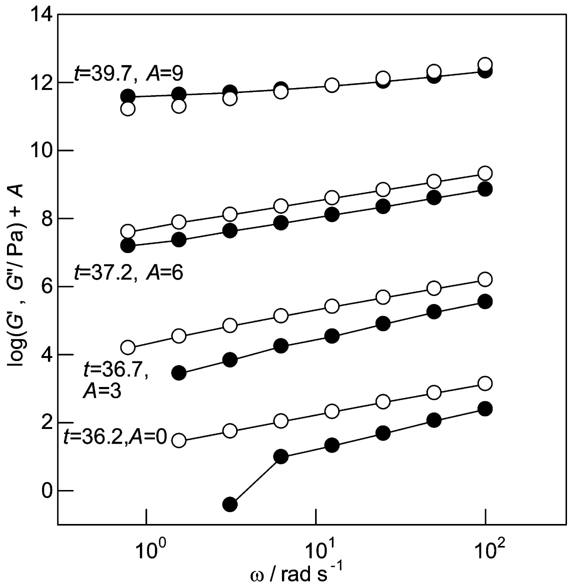

Figure 4. Dependence of G' (filled circles) and G'' (open circles) on angular frequency for the polymerization system of DGEBA and D230($D = 10$), near gel point. The reaction times in min are displayed as *t*. The data are shifted to avoid overlapping by *A* as indicated in the figure.

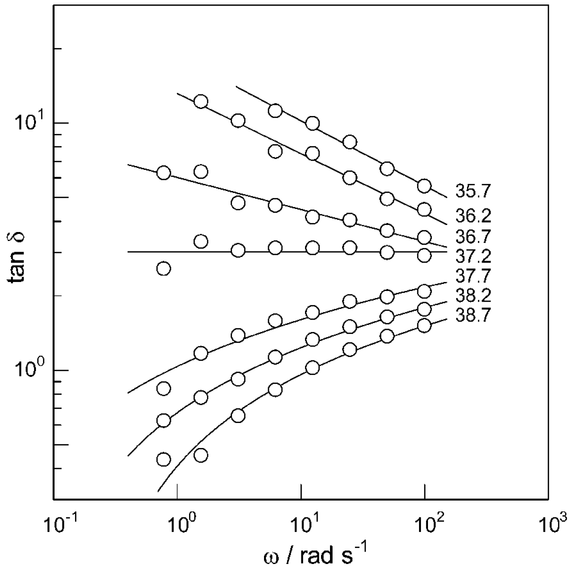

Figure 5. tan δ plotted against angular frequency for the polymerization system of DGEBA and D230($D = 10$), near gel point. The reaction times in min are displayed in the figure. At $t = 37.2$, a frequency independent tan δ is observed.

degree of dilution. All the p vs t plots are fitted with fifth order polynomials for further analyses.

Figure 4 shows the dependences of G' and G'' on the angular frequency, ω in the course of polymerization of DGEBA and D230 of $D = 10$. The data are shifted along the vertical axis by a factor of A in order to avoid overlapping. In the early stage of the reaction, G' is lower than G'' under the frequency range used in this work. With the progress of the reaction, G' approaches to G'' and eventually it exceeds G''. The G', G'' behavior shown in Figure 4 obviously shows the gelation of the system of DGEBA and D230. Furthermore, at $t = 41.7$ min a plateau modulus could be observed for G'. At $t = 37.2$ min, the frequency dependences for both G' and G'' were observed to be proportional to ω^{Δ}, which is known as the power law.[29] As for the gelation of DGEBA with POP diamine, the power law has already been confirmed as $G', G'' \cong \omega^{\Delta}$.[30] Therefore, gelation time can be determined by the time when the power law appeared. It is more easily observed by plotting tan δ against ω, showing a frequency independent tan δ (see Figure 5).

Table 1 summarizes the results of both IR and viscoelastic measurements, and other analytical results as described below. $p_c - p_0$ is the delay from Flory – Stockmayer gel point, p_0 is derived from the general equation of gel point for RA_4+$R'B_2$ type polymerization as $p_0 = 0.577$. The relaxation exponent, Δ, is determined with the following equation.

$$\tan \delta = \tan(\pi\Delta/2) \quad (4)$$

For all the polymerization systems, gelation occurs at the extent of reaction in excess of Flory–Stockmayer gel point, which implies that the ring structures are formed in polymer network. The excesses are 0.09–0.15 in extent of reaction. Furthermore, p_c increases with the dilution, showing that the dilution causes different size of ring structures in the network formation, which will be discussed below. The results agree with

Table 1. Experimental Results for Polymerization Systems Studied[a]

polymerization system		p_c	$p_c{-}p_0$	relaxation exponent	λ_0	u
D230	$D = 0$	0.664	0.087	0.759	0.0276	0.65
	$D = 10$	0.672	0.095	0.799	0.0296	0.67
	$D = 20$	0.716	0.139	0.799	0.0403	0.67
	$D = 30$	0.718	0.141	0.917	0.0410	0.63
	$D = 40$	0.720	0.143	0.823	0.0412	0.63
	$D = 50$	0.730	0.153	0.839	0.0436	0.60
D400	$D = 0$	0.678	0.101	0.817	0.0313	0.68
	$D = 20$	0.683	0.106	0.924	0.0325	0.68
	$D = 30$	0.710	0.133	0.956	0.0389	0.58
	$D = 40$	0.730	0.153	0.879	0.0436	0.55
D2000	$D = 0$	0.667	0.090	0.857	0.0285	0.49
	$D = 10$	0.678	0.101	0.861	0.0314	0.55
	$D = 20$	0.70	0.123	0.890	0.0370	0.50

[a] Key: p_c, critical extent of reaction at gelation; p_0, Flory−Stockmayer gel point; λ_0, ring-forming parameter. Relaxation exponent and u are derived from eq 4 and Figure 7, respectively.

previous data studied for reaction systems forming polyesters and polyurethanes.[31−33]

In spite of some scatterings, the relaxation exponent approximately increases with the degree of dilution, which is consistent with the tendency to decrease the exponent as the increase in cross-linking density reported for poly(dimethylsiloxane) network of the prepolymer with a medium-chain-length.[34] On the other hand, the exponents obtained in this work are slightly higher than the value of $\Delta \approx 0.70 \pm 0.03$ reported for the cure of diepoxy with polyoxypropylenediamine and other low molecular weight diamine.[35] The result of high value might be attribute to the influence of dilution of the reactant.[36]

4. DISCUSSION

According to many research works reported for the curing of the epoxy-amine reaction, the reaction of DGEBA and POP diamine can be analyzed with both catalyzed and noncatalysed mechanism.[37,38] Further, it is shown that the kinetic model requires the consideration of etherification reactions between the glycidyl group and the hydroxyl group produced after the epoxy−amine reaction.[39] However, the analyses of the conversion curves of Figure 2 are devoted to the reactions of the primary amine hydrogen and the secondary amine hydrogen,[24,38,40] since the aim of this work is to estimate the delay of gel points from the viewpoint of the ring−forming parameter. The effect of T_g change on reaction kinetics also adds a further complication to the analyses. As mentioned earlier, T_g of the polymer of DGEBA and POP diamine increases with degree of cure, namely, with the progress of a reaction. It follows that the dynamics of reaction species are suppressed as the reaction progresses, and consequently, some reaction parameters, activation energy or the rate constant ratio(described below) etc., can be affected. The analyzing method to examine these rather complicated processes is also reported for the diepoxy−diamine system.[41]

In this work, the plot of p vs t obtained was examined by the method proposed by Horie et al. to determine the ratio of rate constant, u;[42] that is, $u = k'_2/k'_1$ where k'_1 and k'_2 express the rate constants of the noncatalytic mechanism for the reactions of the primary amine hydrogen and the secondary amine hydrogen, respectively. If k_1 and k_2 are the rate constants for the reactions catalyzed by the hydroxyl groups initially presented in DGEBA and those generated during the reaction, they are denoted as $(HX)_0$ and $(HX)_A$ respectively, the relation of $k_2/k_1 = k'_2/k'_1$ has been accepted. A reaction scheme of eqs 5−8 is set forth, assuming that $(HX)_0$ and $(HX)_A$ act as true catalysts and are not consumed in any side reactions:

$$A_1 + E + (HX)_A \xrightarrow{k_1} A_2 + (HX)_A \tag{5}$$

$$A_1 + E + (HX)_0 \xrightarrow{k'_1} A_2 + (HX)_0 \tag{6}$$

$$A_2 + E + (HX)_A \xrightarrow{k_2} A_3 + (HX)_A \tag{7}$$

$$A_2 + E + (HX)_0 \xrightarrow{k'_2} A_3 + (HX)_0 \tag{8}$$

E, A_1, A_2, and A_3 represent epoxy group, primary amine group, secondary amine group and tertiary amine group, respectively. Let e, a_1 and a_2 be the concentrations of E, A_1, and A_2 at time, t, respectively, e_0 and a_0 the initial concentrations of E and A_1, respectively, c_0 the concentration of $(HX)_0$, and x the the epoxy group consumed after time t.

The changes in the number of reacted H−atoms for the schemes of eqs 5−8 are, in effect, similar to those for the reaction schemes used in the first part. Specifically, both reaction schemes show that two unreacted H atoms are lost and one reacted H atom is formed in the reaction of the primary amine group, one unreacted H atom is lost and one reacted H atom is formed in the reaction of the secondary amine group. Therefore, the concentrations of H atom calculated in the first part are compatible with those appeared in eqs 5−8 with $k_2/k_1 = k'_2/k'_1$. It should be noted that these rate constants are defined on the basis of the concentration of the amine groups, while the rate constants appeared in the first part, k_{H1} and k_{H2}, are based on H atom concentration. They are related as follows; $u = \rho/2$, $k'_1 = 2k_{H1}$ and $k'_2 = k_{H2}$.

We have the following relation,

$$\frac{dx}{dt} = k_1 a_1 e x + k_1' a_1 e c_0 + k_2 a_2 e x + k_2' a_2 e c_0 \tag{9}$$

which can be written,

$$\frac{dx}{dt} = (e_0 - x)(k_1 x + k_1' c_0)(a_1 + u a_2) \tag{10}$$

We also have the relation between a_1 and a_2.

$$a_1 + (a_2/2) = a_0 - (x/2) \tag{11}$$

In addition, the analyses of conversion curves require other variables and their relations; c_{EPR} is the concentration of epoxy group consumed, c_{HR} is that of consumed hydrogen atoms in the amine groups, $c_{EPR} = c_{HR}$ under the experimental conditions of $r = 1$, $(c_{EPR}/c^0_{EP}) = (c_{HR}/c^0_{H1}) \equiv p_{HR}$, then $p_{HR} = p$; also $e_0 = c^0_{EP}$, $c_{EPR} = x$, $a_0 = c^0_{H1}/2$. Finally, these manipulations produce the following relation.

$$\frac{\frac{d}{dt}c_{\mathrm{EPR}}}{(c_{\mathrm{EP}}^{0}-c_{\mathrm{EPR}})\left(\frac{c_{\mathrm{H1}}^{0}}{2}-\frac{c_{\mathrm{EPR}}}{2}\right)} = (k_1c_{\mathrm{EPR}}+k'_1c_0)\left(1+\frac{2a_2(u-0.5)}{2a_1+a_2}\right) \tag{12}$$

Then, the equation to analyze the conversion curve is acquired.

$$\frac{2\frac{dp}{dt}}{(1-p)^2} = (k_1c_{\mathrm{H1}}^{0}c_{\mathrm{EP}}^{0}p+k'_1c_0c_{\mathrm{H1}}^{0})\left(1+\frac{2a_2(u-0.5)}{2a_1+a_2}\right) \tag{13}$$

From the p vs t plot fitted with fifth order polynomial, $2(dp/dt)/(1-p)^2$ was calculated and plotted against p for the polymerizations of DGEBA and D230, D400, and D2000 as shown in Figure 6. The results are comparable with the reduced rate plots reported for the polymerization systems of DGEBA with ethylenediamine (EDA), trimethylenediemine (TMDA) and hexamethylenediamine (HMDA).[42] The plot shows monotonous increase for the first half of the reaction, then, an abrupt fall down follows. The turning points from the monotonous increase to the fall down are different for the reaction systems with different chain lengths of POP. In addition, the slope of the plot decreases and the conversion values at the turning points become lower as the polymerization systems are more diluted. As a propensity, these profiles are similar to the reduced rate plots reported for the reaction systems of EDA, TMDA and HMDA. Deviation of intercepts of the plots from the origin can be attributed to the existence of traces of impurity accelerating the reaction in the system. The effect of impurity on the deviation of intercept is less pronounced by the dilution. From these results, it is shown that DGEBA and POP diamine reacts with the catalytic mechanism as long as the monotonous increase appears.

For the reaction in this work, the concentration of the secondary amine group can be neglected at the initial stage, i.e. $a_2 \approx 0$. Therefore, the terms of $(k_1c^0_{\mathrm{H1}}c^0_{\mathrm{EP}})$ and $(k'_1\, c_0\, c^0_{\mathrm{H1}})$ in eq 13 can be evaluated from the initial slope and the intercept for the individual plot, respectively, taking account of the fact that these parameters are constants. Because the term of $(1 + 2a_2(u - 0.5)/(2a_1 + a_2))$ can be calculated as a function of p,[43] a calculation curve of $2(dp/dt)/(1 - p)^2$ vs p can be constructed by giving possible values of u. In fact, the calculation curves were fitted to the plot of Figure 6 by varying u. The fitting procedures performed were limited within the plot of the monotonous increase, which were approximately with $p < 0.6$ for D230 and D400 systems and with $p < 0.4$ for D2000 system.

The results for various polymerization systems are shown in Figure 7. Also u values determined are shown in Table 1. A large discrepancy is seen in the fitting of the plot of $p > 0.4$ for D230 $D = 10$, showing that eq 13, and hence the kinetic model used in this work cannot be applied to the plot of $p > 0.4$. The polymerization system of DGEBA and D2000 is relatively in slow reaction. The initial slope and the intercept of the plot are much lower than those of D230 and D400 systems. Consequently, the fitting curve of D2000 system came close to the straight line; the effect of the term of $(1 + 2a_2(u - 0.5)/(2a_1 + a_2))$ dropped off, which also affected the u value determination. The error level of 3% is included in u values of D2000 system shown in Table 1. For other polymerization systems, the calculation curve fitted well to the plots of the monotonous increase, and then the determined values of rate constants ratios are likely to be used for further discussion of the gel point.

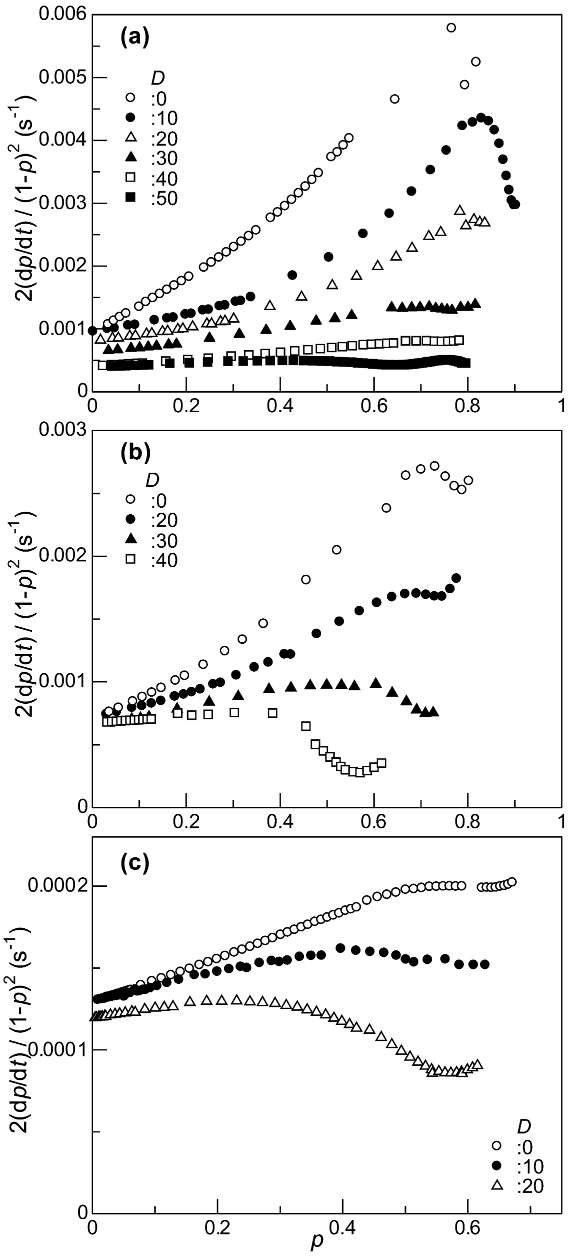

Figure 6. The reduced rate plots (see eq 13) for polymerization systems of DGEBA and D230 (a), D400 (b), and D2000 (c). The degrees of dilution are indicated by D in the figures.

As for the ratio of rate constants, it is usually accepted that u is close to 0.5 as an ideal value for aliphatic amines cured with DGEBA, which comes from the ratio of numbers of reactive groups.[15,44,45] Although values in Table 1 are higher than $u = 0.5$, comparable with those obtained for the reaction system of HMDA of $u = 0.6$–0.7, for Buthylamine of $u = 0.55$–0.73 in spite of slightly higher reaction temperature of 90 °C in this work.[18,44]

As shown in Table 1, λ_0 was determined with $u = \rho/2$ according to the relationship of p_c and λ_0 obtained in the first part.[9] Further, those determined were plotted against $(c^0_{\mathrm{H1}})^{-1}$ in Figure 8 to estimate P_{ab} on the basis of the following relation.

$$\lambda_0 = P_{\mathrm{ab}}/c^0_{\mathrm{H1}} \tag{14}$$

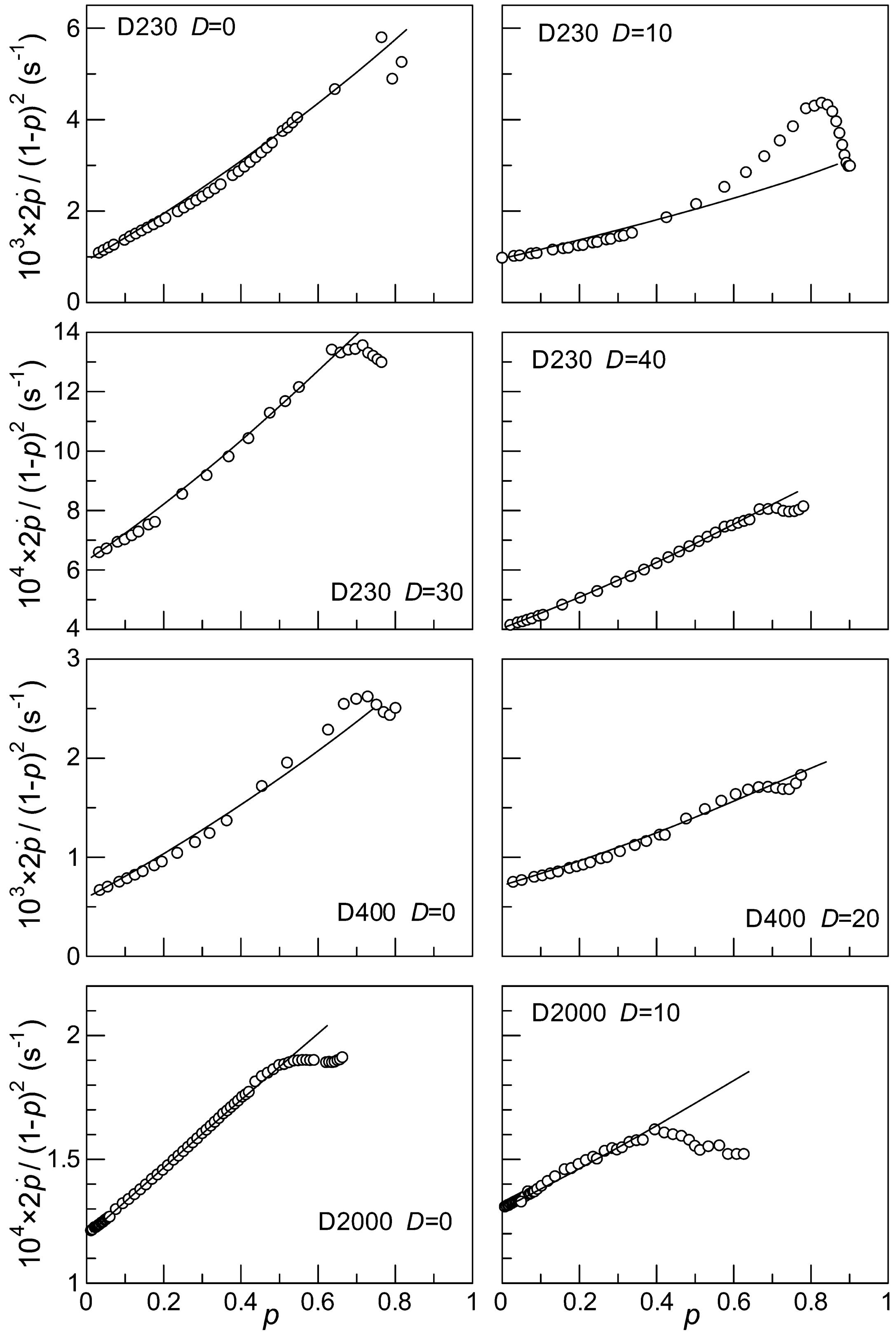

Figure 7. Comparison between the experimental plots and the calculation curves (solid lines) based on eq 13 for the reduced rate plots. POP diamines to show the polymerization systems and the degrees of dilution are displayed in the figure.

The λ_0 vs $(c^0_{\mathrm{H1}})^{-1}$ plots lie approximately on straight lines through the origin which correspond with the Flory–Stockmayer gel point. The slope of the line decreases as the increase in the chain length of POP. The increase in the chain length lowers the density of amine group, and hence lowers the slope of the line corresponding to the concentration of P_{ab}.

The plot implies that the dilution of polymerization solution increased λ_0. More precisely, λ_0 means the ratio between the

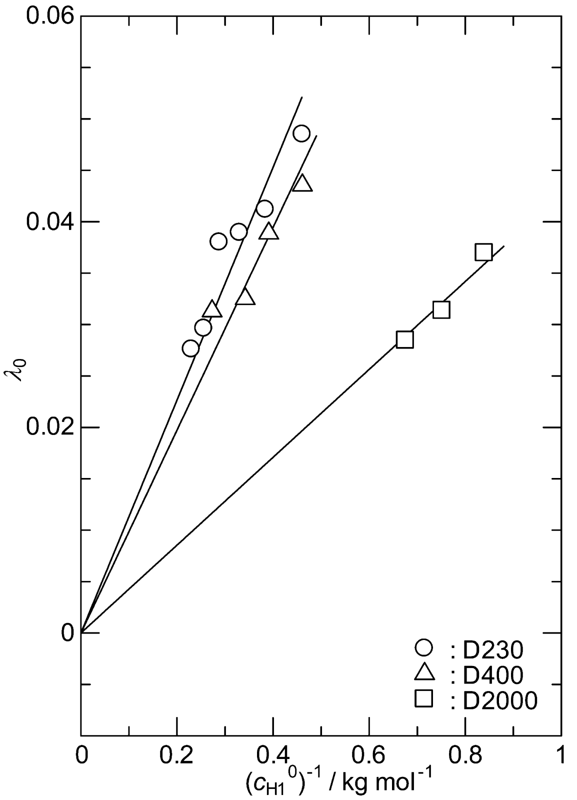

Figure 8. λ_0 plotted against $(c^0_{\mathrm{H1}})^{-1}$ for polymerization systems of D230, D400, and D2000.

internal concentration and overall concentration of reactive groups

$$\lambda_0 = \frac{c_{\mathrm{a,int}}}{c_{\mathrm{a,ext}} + c_{\mathrm{a,int}}} = \frac{c_{\mathrm{b,int}}}{c_{\mathrm{b,ext}} + c_{\mathrm{b,int}}} \tag{15}$$

given that the reactive group ratio is equal to unity, where $c_{\mathrm{a,int}}$ is the internal concentration of A groups (hydrogen atoms in amine groups) from the same molecule around a B group(epoxy group) about to react and $c_{\mathrm{a,ext}}$ is the external concentration of A groups from other molecules. Correspondingly, $c_{\mathrm{b,int}}$ and $c_{\mathrm{b,ext}}$ are the internal and external concentrations of B groups around an A group about to react in the polymerization of RA_{fa} + $\mathrm{R'B}_{fb}$. Dilution of the solution decreases the external concentration while the internal concentration remains the same, which is the reason for increasing of λ_0, and hence the delay of gel point.

Similar results regarding the dilution effect on the delay of gel point can be seen for the reaction systems forming the network of polyurethanes and the interpenetration of epoxy−vinyl ester.[46,47] In addition, in the controlled radical polymerization system of methyl acrylate and ethylene glycol diacrylate, the dilution results in the delay of gel point as evidenced by both MC simulation and ATRP experiments.[48]

Next, the number of bonds was given for the linear sequence of DGEBA and POP diamine units in order to examine b values through eqs 1 and 2 as shown schematically in Figure 9. The repeating unit of DGEBA was neglected because average repeating number is small(n_{BA} = 0.03). Let the number of bonds for DGEBA unit and POP diamine unit be ν_{DGEBA}, $\nu_{\mathrm{POP\ diamine}}$, and the averaged number for repeating unit of POP be n_{POP}, then $\nu_{\mathrm{DGEBA}} = 9$, $\nu_{\mathrm{POP\ diamine}} = 3 + 3 \times n_{\mathrm{POP}}$. The averaged number of bonds for the linear subchain joining DGEBA and POP diamine units (ν_{s}) can be determined with the following equation.

$$\nu_{\mathrm{s}} = (2(\nu_{\mathrm{DGEBA}} + \nu_{\mathrm{POP\ diamine}}) + \nu_{\mathrm{DGEBA}})/3 \tag{16}$$

Table 2 summarizes P_{ab}, ν_{s}, $\langle r^2\rangle$, and b calculated. The value of b for POP linear chain is also added to the table for comparison, which is obtained by the theoretical study of conformational energies using rotational − isomeric state calculations.[49] P_{ab} obtained on the basis of ARS theory is also shown ; ARS theory accounts for the relation of p_{c} and λ_0 in RA_{fa} + $\mathrm{R'B}_{fb}$ type polymerization on the basis of the probability of chain growth between the reactive A group and B group.

Table 2. Polymerization Systems and P_{ab}, ν_{s}, $\langle r^2\rangle$, b Characterizing the Chains Forming the Smallest Loops, and Results of Previous Studies for Comparison

	P_{ab}/mmol L^{-1}				
POP diamine	this work	ARS	ν_{s} (averaged)	$\langle r^2\rangle$/nm^2	b/nm
D230	111.9	148.1	16.4	2.885	0.419
D400	98.6	130.2	22.2	3.137	0.376
D2000	42.7	54.5	77.4	5.480	0.266
linear POP[a]	−		30	−	0.328

[a] Calculated results for atactic POP chains at 80 °C using rotation−isomeric−state theory.

Here, the similarities and differences are described briefly between gel point predictions of ARS theory and this work. The similarities can be seen on the scheme of chain growth caused by the reaction of the hydrogen atom of amine group and the epoxy group, and on the definition of probability of path continuation. The difference is the scheme of unequal reactivity; while ARS theory does not incorporate the unequal reactivity, it is taken into account in this work. The difference can also be seen on the introduction of the classification concerning the state of POP diamine unit. While ARS theory does not incorporate, it is taken in this work. That is, the possibility of forming four paths is given to every POP diamine unit defined in ARS, whereas the exact number of paths is assigned according to the state of reaction in this work so as to calculate the probability of chain growth; for example, the diamine unit having a primary amine and a tertiary amine group has the possibility of forming two paths. Also the fractional concentrations for the respective states of diamine unit are derived as functions of the extent of reaction. Therefore, the gel point calculation of ARS overestimates λ_0. In contrast, the

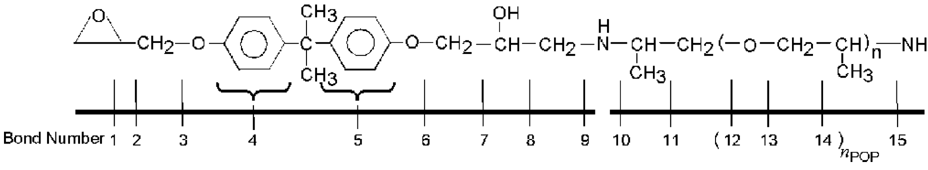

Figure 9. Schematic representation of the linear sequence comprised of DGEBA and POP diamine units to give the number of bonds.

model of chain growth in this work underestimates λ_0 and thus P_{ab}, by introducing detailed molecular structure for POP diamine unit, The overestimation of P_{ab} by ARS is around 30% in comparison with this work as shown in Table 2.

The value of $P_{ab} \approx 100$ mmol/L obtained is roughly the same as that determined in the previous study for the reaction systems based on tetrafunctional POP tetrols and hexamethylene diisocyanate, which are reacted at 80 °C in bulk and at various initial dilutions in nitrobenzene.[50] As mentioned above, P_{ab} decreases with the increase in the chain length of POP diamine. The bond length of the subchain decreases with the chain length; the stiff DGEBA unit results in a larger value of b with shorter chain length of POP diamine unit. Further, b value of POP linear chain obtained for the chain of $\nu = 30$ lies in between those of D400 and D2000. This is acceptable with each other from the viewpoints of the bond number and bond length.

5. CONCLUDING REMARKS

The delay of gel point increased with the degree of dilution for polymerization systems of DGEBA and POP diamine. A total of 9–15% of the reaction is consumed for the delay from the Flory–Stockmayer gel point. The conversion curve of p vs t plot acquired by FT-IR measurements was analyzed on the basis of the general kinetic model for the epoxy–amine reaction. The reduced rate plots obtained are consistent with those reported for other epoxy–amine reaction systems. The ratio of rate constants for the reactions of the primary amine hydrogen and secondary amine hydrogen are given as a plausible value and applied to the further calculation regarding λ_0. λ_0 vs ${c^0}_{H1}{}^{-1}$ plots showed straight lines through the origin which correspond with Flory – Stockmayer gel point. The result of the increase in λ_0 with the degrees of dilution was interpreted with the effect of external concentration seen from the molecule having the reactive groups. P_{ab} was obtained by the gel point calculation developed in the first part of this study. The calculation of ARS theory was also carried out to obtain P_{ab}. The difference of these two calculations is in the scheme of unequal reactivity and the states of the reaction of POP diamine unit. The calculation of ARS overestimates P_{ab} approximately 30% in comparison with the gel point calculation of this work.

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Notes

The authors declare no competing financial interest.

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$((2p_{H2}(1-u))/(p_{H1}+p_{H2}))$. Because p_{HR} is equivalent with p, the term given can be calculated using the relation between p_{H1}, p_{H2}, and p_{HR}.

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