BRANCHING KINETICS OF EPOXY POLYMERIZATION OF
1,4-BUTANEDIOL DIGLYCIDYL ETHER WITH CIS-1,2-
CYCLOHEXANEDICARBOXYLIC ANHYDRIDE

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ABSTRACT: The copolymerization of an epoxy resin [1,4-
butanediol diglycidyl ether (DGEB) (Note a)] with an
anhydride [cis-1,2-cyclohexanedicarboxylic anhydride
(CH)] in the presence of N,N-benzyldimethylamine (CA) as
a catalyst produces a branched epoxy polymer. We show
that the branching kinetics of the copolymerization
reaction and the molecular weight distribution of the
branched polymers can be approximated by using
Smoluchowski's coagulation equation. In the simplest
relevant application of this equation to our problem,
the overall rate kernel w(u,v) that describes the
branching probability in the equation turns out to be
proportional to the sum of active sites on the two
polymers with a time dependent coefficient. The
molecular weight distribution (MWD) and the weight
average molecular weight of the branched copolymers at
different reaction stages before the gelation threshold
are calculated theoretically. The calculated values are
then compared with the experimental results obtained by
using small angle X-ray scattering (SAXS), laser light
scattering (LLS), and chemical analysis. Satisfactory
agreement between experimental results and the use of
the coagulation equation is attained when it is assumed
that the distribution of epoxy polymer molecules is
exponential in the number of branching points or,
equivalently, active sites, at an early stage of the
polymerization reaction.

INTRODUCTION

Highly branched epoxy polymers are produced by the copolymeri-
zation of epoxy resins [for example, 1,4-butanediol diglycidyl
ether (denoted by DGEB)] and an anhydride [for example cis-
1,2-cyclohexanedicarboxylic anhydride (denoted by CH)] with
triamine [N,N-benzyldimethylamine (denoted by CA)] as a
catalyst. In previous articles (Ref.1-4), we have shown how

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*) Address 1 is present address.
Note a: Systematic IUPAC nomenclature: 3,3'-tetramethylene-
dioxydi-1,3-epoxypropane

the three-dimensional epoxy polymer networks are formed. For
the complex curing process (Ref.5), several partially
conflicting reaction mechanisms have been proposed to describe
reaction initiation and the reaction order. In the context of
the present analysis, it is not crucial for us to know how
the reaction is initiated especially when we focus our
attention on the branching kinetics in the curing process. We
shall show that the branching kinetics of the copolymerization
reaction and the distribution of highly branched epoxy
copolymers can be reasonably described by Smoluchowski's
coagulation equation applied in a novel way. The equation has
long been applied to study the structure of the clusters
produced by kinetic aggregation of colloidal particles,
typically <u>with time-independent</u> <u>reaction kernel w(i,j)</u> (Ref.6-
15). Here, instead, we are led to a kernel that describes a
branching probability $w(i,j)$ which is proportional to the sum
of active sites on the two polymers, i.e. $w(i,j) \propto (i+j)$ where
i and j are the number of the active sites on polymers i and
j, respectively, but <u>with a time dependent</u> <u>coefficient of
proportionality</u>. We found that the kinetic equation can be
solved explicitly to obtain the molecular weight distribution
(MWD) and the weight-average molecular weight (M_w) at
different reaction stages.
Experimentally, we used a small angle x-ray scattering (SAXS)
at the State University of New York (SUNY) X21A2 beamline,
National Synchrotron Light Source (NSLS, BNL) and laser light
scattering (LLS) to measure the angular distribution of
absolute scattered intensity ($I(\theta)$) at different reaction
stages. The extent of conversion was determined by the
chemical analysis. From $I(\theta)$, we can determine the weight
average molecular weight. The experimental results were
compared with the calculated values based on an analytical
solution of our modified form of the Smoluchowski coagulation
equation. Satisfactory agreement is obtained when we assume
that the distribution of epoxy polymer molecules is
exponential <u>in the number of branching points (or
equivalently, of active reaction sites)</u> at an early stage of
the polymerization reaction.

BRANCHING KINETICS

The copolymerization of DGEB and CH in the presence of CA is
dominated by alternating linkages between DGEB and CH, i.e.
the reactions between the epoxy resins and between the
anhydrides are suppressed (Ref.16). Highly branched epoxy
copolymers are formed in the copolymerization reaction because

the sum of the reaction functionalities of DGEB (two epoxy rings which can form four chemical bonds) and of CH (one anhydride ring which can form two chemical bonds) is six. This is larger than the gelation criterion, i.e. a minimum total of five functionalities is needed to form a branching point.
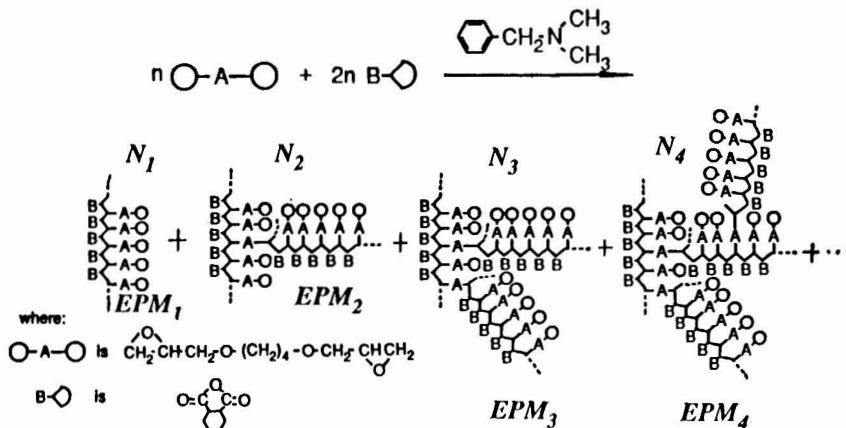

Fig.1. Schematic representation of copolymerization of an epoxy resin (DGEB) and an anhydride (CH). The reaction is dominated by alternative linkages between DGEB and CH. Each N_n unit shown is assumed to include n active sites (not shown) associated with one-half of the 2n terminal positions which are associated with the symbol --- denoting a further linear chain segment. (Note that the n appearing in the coefficients of the reaction displayed at the top of the figure are unrelated to the n denoting active sites).

Figure 1 shows graphically how the branch points are formed in the copolymerization reaction. At the initial reaction stage, most of the polymers formed are linear. As the reaction proceeds, the degree of branching of the branched epoxy copolymer increases (Ref.3). Finally, a three-dimensional network is formed at the gelation threshold.
We know that the triamine CA plays a very important role in initiating the reaction because without triamine as a catalyst, the overall reaction is very slow. But it is not clear how the triamine starts the reaction, i.e. we do not know whether the triamine molecule first reacts with the anhydride molecule or with the epoxy resin. However, when we consider the branching process after the initial reaction stage, it is not important for us to know the exact initial reaction mechanism. For convenience in discussion, let us

adopt Fischer's initial mechanism (Ref.16): the triamine molecule reacts first with the anhydride molecule to form an anion (active site) on the anhydride molecule, the anion further reacts with the epoxy ring on the epoxy resin to form another anion on the epoxy resin, and so on. In Figure 1 one half of the chain segments symbolized by the dashed lines are assumed to be terminated by CA molecules, not shown in the figure.

We shall make our analysis under the following assumptions, which shall subsequently translate into precise quantitative statements:

1) The number of the active sites in the system is constant and equal to the initial number of CA molecules in the system, which can be understood either as no transfer of CA and no termination of the active site at all or a transfer is always corresponding to a termination.

2) The average frequency $f_{TOT}(t)$ with which <u>an</u> active site and <u>an</u> epoxy ring react does not depend on the structure of the molecule upon which the active site is located.

3) Rings do not form during the polymerization process.

Clearly these assumptions define a highly idealized model that describes a process far simpler than the polymerization process of a particular epoxy system under study. As is typically the case when one begins to model a strongly interacting many-particle system, we are looking for the simplest possible model that captures the essential elements of the process we seek to understand and describe.

We shall use <u>the number of active sites n rather than the number of monomers as the key index</u> in describing the evolution of the system. This use is the most novel fundamental feature of our theory and is different from other theoratical approaches. As shown in Figure 1, an epoxy-polymer molecule with n active sites will be denoted by EPM_n. There is an important (approximate) relation between mass distribution and active-site distribution that assures us of experimental access to the information included in our theory. It is

$$m_n \simeq kn \tag{1}$$

where m_n is the mass of an EPM_n molecule and k depends only on time.

Based on assumption 1 and the reaction mechanism described by the remaining assumptions, the number of branching points n_b and the number of active sites in one EPM_n are related by

$$n_b = n - 1 \tag{2}$$

Let us next consider the expression for the average frequency $f(EPM_n)$ with which a given active site reacts with an EPM_n molecule. It follows from assumptions 1 and 2 that $f(EPM_n)$ can be expressed as

$$f(EPM_n) = f_{TOT}(t) \frac{N_n(t)}{N_{EPM}(t) + N_{DGEB}(t)} \qquad (3)$$

Here $N_n(t)$ is the number of EPM_n molecules at time t while $N_{EPM}(t)$ and $N_{DGEB}(t)$ are total number of EPM molecules and number of unreacted DGEB units, respectively, at time t.
During the reaction of an active site with an epoxy ring, a CH unit is consumed. Therefore, the total frequency f_{TOT} with which an active site reacts with an epoxy ring is given by

$$f_{TOT}(t) = \frac{-dN_{CH}(t)/dt}{N_{CA}} \qquad (4)$$

where $N_{CH}(t)$ denotes the number of CH units at time t and N_{CA} is the number of CA, i.e., the number of active site, which is time independent (assumption 1).
For a linear chain, the number of reacted DGEB and CH units is equal. However, when each branching point is formed the active site reacts with an epoxy ring in the polymer and therefore one less DGEB unit is used up in the reaction (when compared with the reaction without branching). Therefore we have:

$$N_{DGEB}(t) = N_{DGEB}(0) - p(t)N_{CH}(0) + N_b \qquad (5)$$

where $\quad p = 1 - \dfrac{N_{CH}(t)}{N_{CH}(0)} \qquad (6)$

is the extent of CH conversion, $p(t)N_{CH}(0)$ is the number of CH molecules used up and N_b is the total number of branching points in the system, which can be simply evaluated from Eq. (2) and assumption 1. Namely, we have

$$N_b = \sum_{n=1}^{\infty} n_b N_n(t) = \sum_{n=1}^{\infty} (n - 1)N_n(t)$$

$$= \sum_{n=1}^{\infty} nN_n(t) - \sum_{n=1}^{\infty} N_n(t) \qquad (7)$$

i.e., $N_b = N_{CA} - N_{EPM} \qquad (8)$

Now, collecting Eqs. (3)-(6) and (8) one gets the following simple expression for $f(EPM_n)$

$$f(EPM_n) = f_A(t)N_n(t) \qquad (9)$$

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where the time-dependant coefficient $f_A(t)$ is defined by

$$f_A(t) = \frac{-dN_{CH}/dt}{N_{CA}N_{CH}(0)[\beta - p(t)]} \tag{10}$$

with $\beta = \frac{N_{DGEB}(0) + N_{CA}}{N_{CH}(0)}$ $\hspace{2cm}$ (11)

Let us now consider the average rate F_{ij} at which molecule EPM_i reacts with molecule EPM_j. According to the assumptions 2 and 3, the rate at which active sites of molecules EPM_i react with epoxy rings of molecules EPM_j equals $iN_i f(EPM_j)$. Similarly for active sites of EPM_j molecules and epoxy rings on EPM_i molecules, the reaction rate equals $jN_j f(EPM_i)$. As a result we get for the total reaction rate

$$F_{ij} = f_A(i+j)N_i N_j \tag{12}$$

In Eq. (12) we have omitted the argument t for notational simplicity. It is obvious that $F_{i,j} = F_{j,i}$. Now we consider how N_n changes with reaction time. If an active site on EPM_n molecules reacts with an epoxy resin DGEB, the result is an increase in the length of an EPM_n molecule but N_n will not change. N_n changes only when the epoxy polymer molecules react with each other. The change in N_n consists of two parts: an increase in N_n when an EPM_i molecule reacts with an EPM_j molecule where $(i + j) = n$ and a decrease in N_n when an EPM_n molecules reacts with any other epoxy polymer molecule. Based on the above conditions, we find the reaction rate to be

$$\frac{dN_n}{dt} = \frac{1}{2} \sum_{i+j=n} F_{i,j} - \sum_{i=1}^{\infty} F_{n,i} \hspace{1cm} n = 1,2,\ldots$$

$$= \frac{1}{2} \sum_{i+j=n} f_A(i + j)N_i N_j - \sum_{i=1}^{\infty} f_A(n + i)N_n N_i, \tag{13}$$

Let us compare Eq. (13) with the Smoluchowski coagulation equation (Ref.17):

$$\frac{d\nu_n(t)}{dt} = \frac{1}{2} \sum_{i+j=n} K_{i,j}\, \nu_i \nu_j - \nu_n \sum_{i=1}^{\infty} K_{n,i}\, \nu_i \tag{14}$$

where $K_{i,j}$ is the overall collection probability and $\nu_n(t)$, with $n = 1,2,\ldots,\infty$, is the concentration of n-size "droplets". The "droplets" could be any cluster of particles undergoing coalescence, e.g., cloud droplets, colloidal particles and so on. It is not difficult to see that Eq. (13) has the same form as Eq. (14) if we let $f_A(i + j) = K_{i,j}$. When the overall collection probability $K_{i,j}$ is proportional to the sum of

"droplet volumes" and is independent of time, i.e. $K_{i,j} = b(i + j)$ with b being a constant, Eq. (14) has known explicit solutions for certain initial conditions (Ref.18-21). For our copolymerization process, however, we cannot directly solve Eq. (14) because f_A is not a constant with respect to time. We have to rearrange Eq. (13). By using the definition of f_A and p, we can transform $f_A dt$ as $d\varsigma$ by using the definition of f_A, according to Eq. (10), with

$$\varsigma = \frac{1}{N_{CA}(0)} \ln(\frac{1}{\beta - p})$$ (15)

With Eq. (15), we rewrite Eq. (13) as

$$\frac{dN_n}{d\varsigma} = \frac{1}{2} \sum_{i+j=n} (i + j)N_i N_j - \sum_{i=1}^{\infty} (n + i)N_n N_i$$ (16)

By comparing Eq. (16) with Eq. (14), we now have $K_{i,j} = (i+j)$ with b = 1. For the initial condition, possible transfer and termination of active sites have to be considered, because, from experimental observations, the molecular weight distribution of the epoxy polymer formed is polydisperse, even in the very early reaction stages. Therefore, a simple exponential distribution on the number of EPM_n formed at some initial extent of conversion p_o was assumed.

$$N_n(p_o) = \frac{N_{EPM}(p_o)}{\bar{n}(p_o)} \exp(-\frac{n}{\bar{n}(p_o)})$$ (17)

where $N_{EPM}(p_o)$ and $\bar{n}(p_o)$ are respectively the total number of epoxy polymer molecules at p_o and the mean active site per epoxy polymer molecule at p_o. For this particular type of initial condition, Golovin (Ref.18) and Scott (Ref.19,20) have shown that Eq. (16) can be solved by using Laplace transforms and a conformal transformation, yielding an exact solution

$$N_n(p) = \frac{N_{EPM}(p_o)}{\bar{n}(p_o)}(1 - \frac{p-p_o}{\beta-p_o})\exp[-(\frac{p-p_o}{\beta-p_o} + 1)\frac{n}{\bar{n}(p_o)}]$$

$$\sum_{m=1}^{\infty} \frac{(\frac{p-p_o}{\beta-p_o})^m [n/\bar{n}(p_o)]^{2m}}{(m+1)!m!}$$ (18)

We have to point out that Eq. (17) is not a unique choice for the initial condition. However, it is perhaps the simplest tenable distribution that can be handled analytically, permitting us to introduce M_w/M_n at some early time t_o (or equivalently, early extent of conversion p_o) as a parameter that can be adjusted to be consistent with the observations.

EXPERIMENTAL METHODS

MATERIALS: The epoxy resin DGEB (M_w= 202.3 g/mol) and the anhydride CH (M_w = 154.2 g/mol) were purchased from Aldrich Chemical Company and used without further purification since selected experimental results were unchanged after both components were purified by vacuum ($\approx$0.01 mm Hg) distillation. The catalyst CA, courtesy of Gary L. Hagnauer, Polymer Research Division, Army Materials Technology Laboratory, Watertown, Mass., was vacuum distilled before use.
PREPARATION OF SOLUTIONS AND METHODS OF MEASUREMENT: The method of preparation of the reaction mixture and of the sample solutions for light scattering has been described in detail elsewhere (Ref.2,3). The light-scattering spectrometer has also been described in detail in previous papers (Ref.2,22).

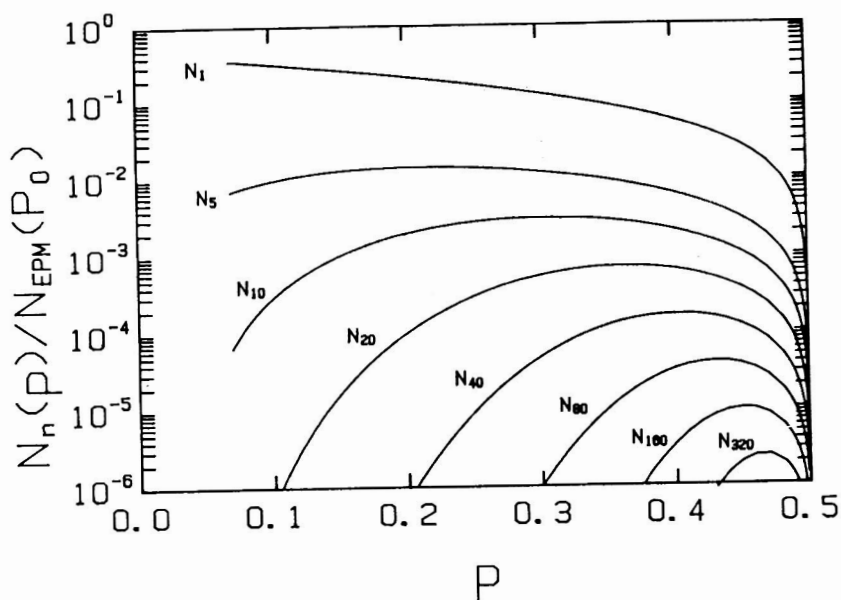EXPERIMENTAL RESULTS AND DISCUSSION

Fig.2. Plot, according to Eq.(18), of calculated number of epoxy polymer molecules with n branching points, i.e., n active sites, (N_n) versus p for different values of n but the same initial molar ratios of DGEB:CH:CA = 1:2:0.001, $\bar{n}(p_o)$ = 1 and p_o = 0.065.

By means of the chemical analysis (Ref.23), we monitored the extent of CH conversion during the copolymerization reaction, i.e., p(t).

From Eq.(18), we can calculate the number of epoxy polymer molecules with n branching points (N_n) (i.e., n active sites) with different extent of conversion (p) for the copolymerization reaction.

Figure 2 shows how $N_n(p)$ change with p for the initial molar ratios of DGEB:CH:CA = 1:2:0.001, $\bar{n}(p_o) = 1$ and $p_o = 0.065$. We also note that N_1 always decreases as the reaction proceeds and there is a maximum number of molecules for each of the other types of molecule during the copolymerization process. The maximum is shifted to $p = \beta$ when $n \to \infty$.

By assuming that all catalyst molecules start the polymerization reaction at the same time, each subpolymer chain will grow at the same speed and produces the same linear length (l_o). The molecular weight for the subpolymer chain (l_o), denoted as $M(l_o)$, should be the total reacted weight divided by the number of active sites (i.e. $N_{CA}(0)$).

$$M(l_o) = \frac{p \, N_{CH}(0) \, (M_{DGEB} + M_{CH})}{N_{CA}(0)} + M_{CA} \qquad (19)$$

where M_{DGEB}, M_{CH} and M_{CA} are the molecular weights of DGEB, CH and CA, respectively. In this way, each EMP_n molecule has n such subpolymer chains. The molecular weight for EPM_n molecule should be n times $M(l_o)$, i.e. $M(EPM_n) = nM(l_o)$ which represents a consequence of our stringent assumptions. Using the definition of weight distribution, $f_w(M)$, and together with Eq. (18) and (19), $f_w(M)$ at different p can also be expressed as

$$f_w(M) = \frac{M(EPM_n)N_n(p)}{\sum_{n=1}^{\infty} M(EPM_n)N_n(p)} = \frac{nM(l_o)N_n(p)}{\sum_{n=1}^{\infty} nM(l_o)N_n(p)} \qquad (20)$$

Figure 3 shows the calculated $f_w(M)$ at different conversion p where we have chosen $M_w(p_o) = 4.1 \times 10^3$ (g/mol) and $\bar{n}(p_o) = 1$ at $p_o = 0.065$, which is the lowest experimentally measured molecular weight. The reason for setting $\bar{n}(p_o) = 1$ is that most of the epoxy polymer molecules formed in the initial reaction stage are linear (Ref.1-4).

In Figure 3, we see that the molecular weight distribution is spreading as the reaction approaches the gelation threshold.
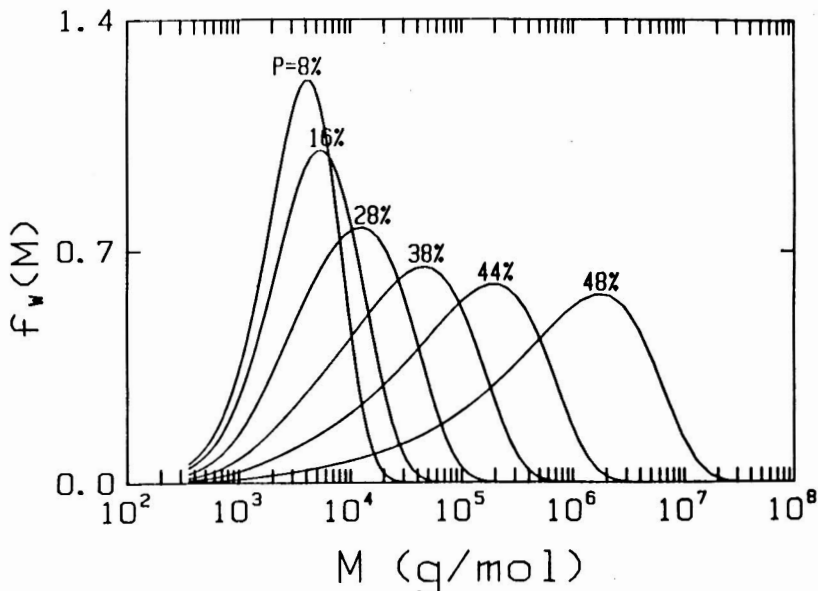
Fig.3. Plot of calculated weight distribution ($f_w(M)$) versus M at different extent of conversion p from Eq.(18)-(20). p_o = 0.065, $\bar{n}(p_o)$ = 1, and DGEB:CH:CA = 1:2:0.001.

From Eq.(20) and the definition of the weight-average molecular weight (M_w), i.e. $M_w = \Sigma M f_w(M)/\Sigma f_w(M)$, we can calculate M_w at each reaction stage. The continuous line in Figure 4 shows such a calculated result at a fixed molar ratio of DGEB:CH:CA = 1:2:0.001. The measured M_w versus p (represented by the hollow squares) for the reaction mixture at the same fixed molar ratio is also plotted in Figure 4. The agreement between the calculated curve and measured M_w values is fairly good.

Our results show that in treating polymerization problems one can introduce the Smoluchowski equation in a form <u>in which the index n of N_n is not simply the number of monomeric units but the number of branches</u>. By using an exponential distribution, we can predict the nature of the epoxy polymer product from knowledge of the initial stages of the polymerization process. Düsek et al.(Ref.24) have discussed a statistical branching theory in an analysis of gelation of a similar system, diepoxide-cyclic anhydride-tertiary amine. However, their emphasis was mainly on the critical extent of conversion at gelation. A more general form for the reaction kernel and the

initial distribution can also be considered. Further experimental and theoretical studies should be a worthwhile undertaking.
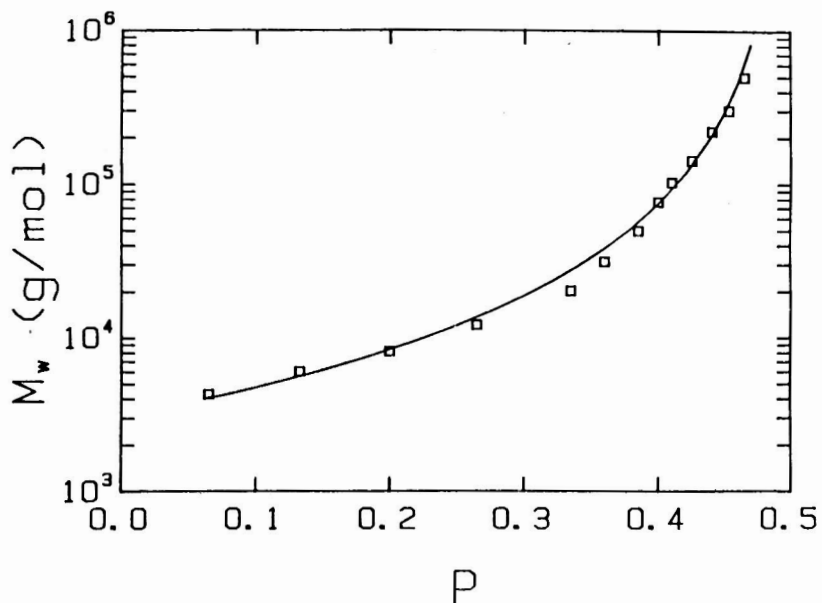

Fig.4. Plot of weight-average molecular weight M_w versus p. Solid line: calculated values using Eq. (30) where p_o = 0.065, $\bar{n}(p_o)$ = 1, and DGEB:CH:CA = 1:2:0.001. Squares: experimental data for the same ratio of DGEB:CH:CA at 80°C.

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