Gel Degradation Theory. 1. An Experimental Verification with a Model Trifunctional Network

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ABSTRACT: The gel degradation theory is discussed according to a conceptual approach which basically reverses the process of gelation. In this context, the major experimental requirements are described for simulating network degradation in a manner analogous but exactly opposite to gelation. Networks formed by the condensation of 1,3,5-benzenetriacetic acid (BTA) with 1,16-hexadecanediol (HDG) when swollen in THF and then degraded hydrolytically produced soluble fractions which quantitatively confirmed the gel degradation theory. The molecular weights ($\bar{M}_w$) of the soluble fractions exhibited progressively increasing values as degradation proceeded. They correlated quantitatively with theoretical values obtained by applying the gelation statistics in reverse. The molecular weight distributions of these sols were of a deceptively similar but highly skewed nature throughout the process, a feature which fully supports the theory. Furthermore, these degradation samples were qualitatively identical (in terms of species distribution) with those isolated during polymerization beyond the gel point. Kinetically, degradation accorded quantitatively with Gardner's model. The results constitute strong evidence that random network degradation proceeds in a manner analogous to the reverse of network formation.

Introduction

Considerable research has been devoted to exploring degradation processes taking place during the processing, use, and aging of macromolecular substances. Most of the work published so far has primarily examined the various modes of degradation of linear macromolecules. Little attention has been given to the degradation of three-dimensional polymer networks, especially from an experimental point of view.

Analytical methods currently available for the chemical investigation of the degradation of polymer networks are often limited. The inherent insolubility of networks provides one major limitation. Furthermore, quantitative conclusions related to the structure or the mode of degradation of polymer networks are difficult to access because chemical or spectroscopic investigations of the concentration of cross-links are generally not sensitive enough; only minor changes in concentration cause marked alterations in the network structure.

Perhaps for these reasons, theoretical and experimental efforts in the field have been restricted to formulating theories and to making measurements which follow the macroscopic physical changes in the network that are brought about by chemical degradation. The degradation of networks formed by the cross-linking of preformed polymer chains (i.e., vulcanized rubber) has been dealt with almost exclusively by these methods. Stress-relaxation studies and swelling measurements have been used for this purpose. The force required to maintain a sample at constant elongation during degradation is a measurable quantity. This force changes with overall macroscopic changes occurring during network degradation. Theoretical expressions relating network parameters to stress relaxation phenomena and to the swelling capacities of networks during degradation were originally derived by Charlesby,[1] Tobolsky et al.,[2] Berry and Watson,[3] Watson,[4] and Horikx.[5] More extensive reviews on the subject can be found in the dissertations of Allen[6] and Gates[7] who investigated the degradation of rubber vulcanizates by these techniques.

Such techniques, however, were beyond the original objective of the present work, i.e., to determine whether network degradation is the reverse of polymerization.[8,9] This primary objective required that attention be paid to the solubilized material as it progressively formed during random network degradation. Thus, molecular weights and molecular weight distributions of these soluble fractions were the quantities of interest. As such a theoretical treatment attempting to formulate these quantities during degradation will be based on applying network formation theories in reverse. Such studies are of particular significance in the industrially important solubilization process of the natural polymer lignin (the wood delignification process). It is, therefore, no surprise to find that work on these aspects of network degradation have been undertaken exclusively by lignin chemists.

Szabo and Goring[10] were the first to assume that gel degradation is the reverse of polymerization. They treated delignification as the reverse of polymerizing a mixture of difunctional and trifunctional monomers based on the Flory–Stockmayer theory. By postulating the concurrent degradation of two gels, they obtained good agreement between the theoretically predicted behavior and their experimental results. The gel degradation theory provided a reasonable explanation of the patterns of increasing molecular weights of the solubilized lignins with increasing degree of delignification. The conclusions of Szabo and Goring, however, are distinct from those of Bolker and Brenner,[11] who treated delignification as the depolymerization of a network composed of relatively short polymer chains joined by frequent cross-linking groups. The calculations of Bolker and Brenner suggested that 5 out of 18 monomer units in lignin (on the average) bore cross-linking groups. The average degree of polymerization of the primary chains was estimated to be 18. (To simplify the calculation, they treated the primary chains as monodisperse.) Yan and Johnson[12] have compared and discussed, from a theoretical point of view, the postulates of Szabo and Goring, on the one hand, and of Bolker and Brenner, on the other.

In two previous papers, we have critically examined the applicability of the available theories on postgel relationships.[8,13] This examination has provided the background for attempting to qualitatively and quantitatively test the validity of the assumption that network degradation is the reverse of polymerization. More specifically, an attempt

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is made here to test the basic premise of the Szabo and Goring model.

Berry[14] was the first to attempt to confirm the gel degradation theory by degrading polyester networks formed by condensing 1,3,5-benzenetriacetic acid with 1,10-decanediol (BTA/DMG). On progressive degradation of the polymer network, swollen in methanol, Berry produced soluble fractions in increasing yields as predicted by the theory. The gel premeation chromatograms of his samples showed that the high molecular weight components of the distributions increased with degree of degradation, while the low molecular weight species diminished progressively. With respect to the weight-average molecular weights of these sols, however, the results agreed only qualitatively with the theory.

The hydrolytic degradation of commercially important polyester networks, as well as other networks, has been studied in the past,[15-18] but never for the purpose of confirming the gel degradation theory. Before the work of Berry, only Gardner[19] attempted to correlate the gel degradation theory to kinetic dissolution data obtained from the acid hydrolysis of Sephadex, a cross-linked polysaccharide. The mathematical model thus derived predicted acceleration of the degradation rates as degradation proceeded. It also predicted that the molecular weight of the dissolved material increased with extent of degradation. The experimental kinetic data, however, were found to seriously deviate near the end of degradation. It was possible, however, to interpret the results as a qualitative confirmation of the gel degradation theory, at least in its kinetic aspects.

With the work of Berry and of Gardner as a background as well as the earlier investigations of Szabo and Goring[10] and of Bolker and Brenner,[11], the present investigation was undertaken to determine whether a quantitative fit to the gel degradation theory could be obtained.

The product of the reaction of 1,3,5-benzenetriacetic acid (BTA) with 1,16-hexadecanediol (HDG) was the network whose degradation was chosen for investigation. The work in this paper deals with the examination of the random degradation of a gel produced by the polycondensation of a polyfunctional molecule ($f = 3$) with a difunctional one.

Experimental Section

A large batch of BTA/HDG network polymer was prepared by polymerizing 5.0400 g of predried 1,3,5-benzenetriacetic acid (synthesized as described in ref 13) with 7.7535 g of predried 1,16-hexadecanediol. The procedure was similar to that described elsewhere,[20] with the following minor modifications. It was of great importance to achieve complete melt homogenization prior to the gel point. For this reason, the polymerization tube containing the carefully weighed monomers was immersed (under nitrogen) at 180 °C until the diol and BTA had been totally mixed and homogenized (with the aid of a small magnetic stirrer). Only then was the temperature of the oil bath lowered to 160 °C. The amount of water evolved was monitored at regular intervals. The polymerization was stopped when 98.5% of the theoretical amount of water had been liberated. Prior to degradation, the network was pulverized, and the residual sol was exhaustively extracted with THF as follows.

The polymer contained in a 250-mL beaker was allowed to swell overnight in THF. It was then carefully crushed in the beaker by applying pressure on it in a circular motion with the bottom of a 100-mL volumetric flask. The 100-mL volumetric flask (Pyrex USA No. 5640) fits almost tightly in the 250-mL beaker (Pyrex USA No. 1000) in the presence of solvent and the swollen gel. The circular motion and pressure applied provided constant recirculation of the gel, thus effecting homogeneous pulverization. The pulverized gel was then Soxhlet extracted with THF for 24 h.

This extraction never produced more than 0.1% of sol. In any case, it was done because one could not calculate what the effect of polymerization sol species would be on the molecular weight of the degradation sols if the polymerization sols had been present during degradation. The pulverized, sol-free network polymers were air dried for 24 h and then were brought to constant weight by heating in a vacuum oven set at 55 °C overnight and storage in a vacuum dessicator over KOH at 10^{-3} mmHg over a period of 2 weeks.

Network Degradation. An accurate weight ($\simeq$0.5 g) of the predried, pulverized, sol-free BTA/HDG network was swollen in a beaker, for 1 week in 20 mL of methanol (for the experiments in methanol) and overnight in 10 mL of redistilled THF (for the experiments in THF). The beaker was covered with aluminium foil and with wax paper surrounded by a rubber band so as to prevent evaporation of the solvent. Network swelling was allowed to proceed under mild stirring with the aid of a small magnetic follower. The addition of 10 mL of sodium methoxide solution, 0.183 M (prepared by dissolving pure sodium in methanol under nitrogen), would commence network degradation. Throughout the experiments reported in this work, the same batch of MeONa solution and of BTA/HDG network was used. The extent of degradation from sample to sample was varied by varying the time during which the network was in contact with the MeONa reagent. At the end of the specified degradation period, the reaction was terminated by the addition of regenerated strongly acidic ion-exchange resin Dowex 50W-X8. Prior to isolating the sol, the mixture was stirred for 10–15 min in order to ensure full exchange of the basic species. A pH meter was actually found to be useful for monitoring the ion-exchange process.

Isolation of Degradation Sols. The sol isolation procedure was applied immediately after the degradation procedure. The sols were never allowed to remain in contact with the ion-exchange resin for more than 10–15 min. The mixture of ion-exchange resin, undegraded network, and swelling medium was filtered through a fine porous filter funnel (preferably without vacuum application) into a round-bottom flask. The residue was then washed with 3 × 20 mL of predistilled THF and the extracts were evaporated to dryness as soon as possible. The network residue was then quantitatively transferred from the porous funnel into a beaker and was mixed with 50 mL of predistilled THF. Any residual sol species were further removed by stirring the mixture overnight. After filtration into the original sol sample, the process was repeated. This ensured quantitative removal of sol from the network. The weight of sol is a critical quantity in degradation experiments, as it is further used to calculate the degree of reaction. The thus isolated dry sol was dissolved in predistilled THF so as to give $\simeq$1% w/v solution. The solution was then quantitatively filtered through a 0.5-μm Millipore-type FG filter (Waters Associates) into a predried, preweighed, round-bottomed flask. After removal of the solvent, the sol sample was dried in a vacuum desiccator over KOH at 10^{-3} mmHg to constant weight. For total removal of the solvent, a drying period of up to 2 weeks was required. Instrumental analyses were performed with the instruments previously described.[8,21]

Results and Discussion

According to the gel degradation theory low molecular weight fragments are initially cleaved from the network as it is randomly degraded. The size of the fragments progressively increases, however, in a way that the process is the reverse of gelation. This occurs because as the degradation proceeds, the probability increases that a larger number of bond cleavages will have occurred that are required to detach larger fragments. The nature of a three-dimensional polymer network is such (especially a network formed by condensing an RA_f with a BB molecule, where $f = 3$) that on random bond cleavage, initially most of the bond scission will be less effective in producing sol molecules. Therefore, early in the degradation, small amounts of low molecular weight fragments are expected to be detached from the network. At the latter stages of the degradation process, however, the bond cleavage reactions become progressively more effective in freeing sol molecules of progressively increasing size. At this stage, fewer bonds need to be cleaved to free larger fragments

Table I
Degradation of BTA/HDG Networks Swollen in Methanol

experimental values			calculated values			
degradation time, h	wt % sol isolated	$\bar{M}_w \times 10^{-5}$,[a,b] g mol^{-1}	dn/dc, mL g^{-1}	W_S[c]	d[c]	$\bar{M}_w \times 10^{-5}$,[d] g mol^{-1}
2.0	4.7	0.037	0.1108	0.0502	0.135	0.0124
3.0	25.0	1.070	0.0816	0.2695	0.216	0.0321
3.5	34.4	1.450	0.0825	0.3690	0.233	0.0440
4.0	55.3	2.010	0.1055	0.5820	0.260	0.0831
6.0	73.7	2.360	0.0952	0.7600	0.276	0.1680

[a] For comparison the theoretical $\bar{M}_w$ values are given at the same value of d. [b] Determined by GPC/LALLS; average of two runs. [c] Calculated according to the procedure described in the Appendix. Critical point $d_c = 0.293$. [d] Using eq 1 of ref 8; setting $M_{Af} = 294$, $M_{B_2} = 258$, $M_c = 32$, $f = 3$, $r = 1$.

from a less densely cross-linked network.

This description really represents an attempt to put into words the network-forming process in reverse. It has been shown[21] that during network formation, the sol species of highest molecular weight are preferentially attached to the gel (the effect becoming more pronounced closer to the gel point). The gel degradation theory requires that as the gel approaches the degelation point, sol species of increasing molecular weight are detached.

For the experimental simulation of network degradation in a way exactly analogous and reversible to gelation, the following conditions should be closely adhered to. They are really assumptions required for formulating the gel formation theory (once again applied in reverse): (1) Bond cleavage should be specific and totally random. (2) The rate of bond cleavage should be equal in both the network and the detached soluble species.

The first condition, requiring the simulation of the process on a purely stochastic basis (assumption of total randomness), appears simple but actually is difficult to achieve experimentally. The degradation reagent must be present throughout the mass of the network at all times during the process, so that it can cleave bonds as efficiently in the center as on the surface. In other words the solvent and degradation reagent should have free access to all parts of the network. This condition implies that the network must be sufficiently swollen that all bonds are equally accessible. An enhancement in the swelling capacity of a network (for the purposes of this investigation) implies facilitation of the processes of reagent absorption into the reaction site and of desorption of the product into the bulk liquid. Both such processes, when operating, would probably be diffusion controlled, thus violating the condition of randomness and rendering the experimental data unsuitable for comparison with the degelation theory. These considerations lead to the following experimentation aimed at simulating random network degradation in a manner analogous but exactly reversible to random network formation.

Network Degradation in Methanol. The degradation procedure adopted by Berry[14] was the first attempted in the present investigation, the only difference being in the composition of the networks. Finely pulverized BTA/HDG networks, which had been polymerized to very near completion, were swollen in methanol and degraded with dilute sodium methoxide solution (0.183 M) for various lengths of time. The resulting degradation sols appeared as white precipitates in the methanol, although they were soluble in THF. Samples of successive degradations were then examined by gel permeation chromatography/low-angle laser light scattering photometry (GPC/LALLS), as reported elsewhere.[21] Figure 1 shows the instrumental output obtained in this series of experiments.

The refractive index (RI) detector of the GPC produced a series of chromatograms which were actually very similar in appearance, the difference being mainly in the high

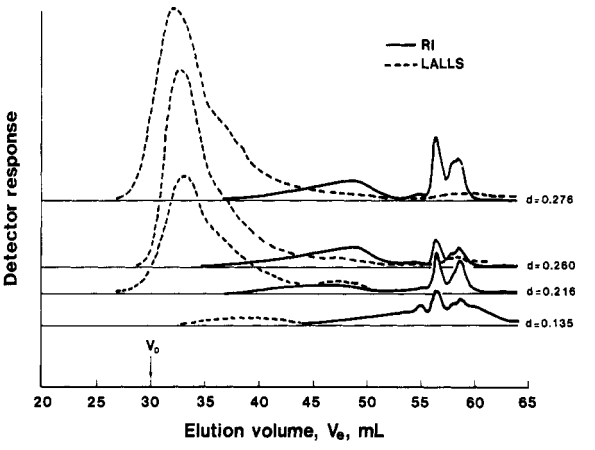

Figure 1. GPC/LALLS combined outputs for successive BTA/HDG network sols as obtained by degrading the gels swollen in methanol (columns used, μ-Styragel (Waters) in the sequence 10^6–10^5–10^4–10^3–500 Å), where d = degree of network degradation.

molecular weight tailing observed with increasing extent of degradation. The significant feature of this series of results is the extensive light scattering (LALLS) response over areas of the RI detection curve for which almost no RI response was observed. This effect might be attributed to the presence of microgel particles within the examined samples, but extreme care had been exercised to remove microgel particles. The samples had been microfiltered (0.2 μm) and centrifuged at 12×10^3 rpm for 1 h.[8] As an additional precaution, a 0.5-μm filter had also been used ahead of the columns in the chromatograph to exclude the possibility of any large particles entering them and passing through to the detection cells.

It is quite certain, then, that the response shown in Figure 1 can only be attributed to an extremely heterogeneous material. Qualitatively, it is this kind of heterogeneity that one would expect from the random degradation of a polymer network. Bolker, Rhodes, and Lee[22] rationalized the similarity of their chromatograms of various soluble fractions resulting from the random network degradation of lignin on the basis that they all represented broad and highly skewed distributions. The present results fully justify this rationalization, although only on a qualitative basis. The position of the maxima of these distributions was not expected to change substantially with degree of degradation. Furthermore, the nature of the polymeric species within these degradation sols is such that hydrodynamic variations with molecular weight were expected to be minimal, as has been shown by viscosity measurements on similar samples.[23] These considerations demonstrate that refractive index detection alone on a gel permeation chromatograph is inadequate for the purpose of visualizing distributions in gel degradation sols. Figure 1 shows that there was a wide range of molecular sizes among the sol samples isolated by degrading the BTA/HDG networks and that they had a

broad weight fraction distribution. This distribution could only be made visible by combining LALLS detection with RI detection to follow the size-exclusion process.

Calculation of the weight-average molecular weights of the sols obtained in this series of experiments gave the results in Table I. As in previous experiments[8] the refractive index (dn/dc) incremental change with concentration for each sample was determined separately, and the second virial coefficients were taken as 5×10^{-5} mol mL g^{-2}.[14]

The results in Table I give only qualitative support for the gel degradation theory. The molecular weights of the successive degradation sols increased with increasing sol yields (W_S) as degradation progressed. This observation accorded with Berry's results on his BTA/DMG gel degradation experiments in methanol. Except for an early fraction, taken at $d = 0.135$, there was no agreement between experimental molecular weights and their theoretical values derived by applying the gelation equation for the postgel region.[8]

A significant source of the error in these experiments may have been the phase separation of the soluble species detached from the network during degradation. These species appeared as a precipitate which increased in amount with increasing degree of degradation. As a result, the second experimental requirement for degradation (previously outlined) was not fulfilled: the rate of bond cleavage within the sol and the gel should be equal throughout the process. The detached sol fragments needed to remain in solution to be further cleaved by the degradation reagent.

The need for this requirement becomes plain on critical examination of polymerization beyond the gel point[8,13,21] and how it should occur in reverse. During polymerization beyond the gel point, simple sol molecules react with each other, producing sol species of higher functionality. Their higher functionality and complexity makes them more likely to participate in sol–gel reactions than in sol–sol reactions. As already shown,[21] the network grows at the expense of such sol entities of higher molecular weight. They are the ones that are preferentially attached to the gel phase. In principle, the polymerization should stop if these soluble species are effectively not allowed to participate in the process. On degradation, therefore, the opposite should be allowed to occur: all sol molecules detached from the gel should be allowed to further cleave to simpler species in the same way that simple sol species combine together during gelation. In other words, even after the sol is generated, it should be allowed to react throughout the degradation process. Only then can its molecular weight be compared with that derived from equations originally intended for gelation.

In the experiments described so far, the use of methanol as the swelling medium caused precipitation of the sol, which effectively removed and protected it from any subsequent degradation. Therefore, their molecular weights are considerably higher than those predicted by the gel degradation theory. Gardner[19] calculated the differences expected between the weight-average degrees of polymerization of a sol obtained by the degradation of a gel in batch degradation and those of a sol obtained by a degradation from which the sol is continuously removed. The results of his calculations accord with the preceding discussion.

One may argue, however, that even from an experiment in which the sol is continuously removed, the "real" molecular weights of the fragments are easily accessible by calculation. The molecular weights of each individual fraction can be combined according to their weight fractions and the cumulative value can thus be obtained. This method, however, will still produce values higher than theoretically predicted. The deviation becomes increasingly apparent as the reaction approaches the degelation point. This occurs because a high molecular weight fragment removed from the reaction at any stage would contribute differently to the overall molecular weight than if it were allowed to be present and further cleaved. The weight-average molecular weights are more susceptible to such errors as the reaction approaches the degelation point, where the weight fraction of the high molecular weight component of the distribution is expected to assume higher values. As already pointed out (for gelation),[8,9,21] and as now seen in degradation, it is the high molecular weight components of the sol distributions that determine the gradual change in the weight-average molecular weights of the sols. Therefore, experiments to examine the reversibility of the gelation statistics must be carefully designed to preserve the "real" size and weight fraction of these fragments.

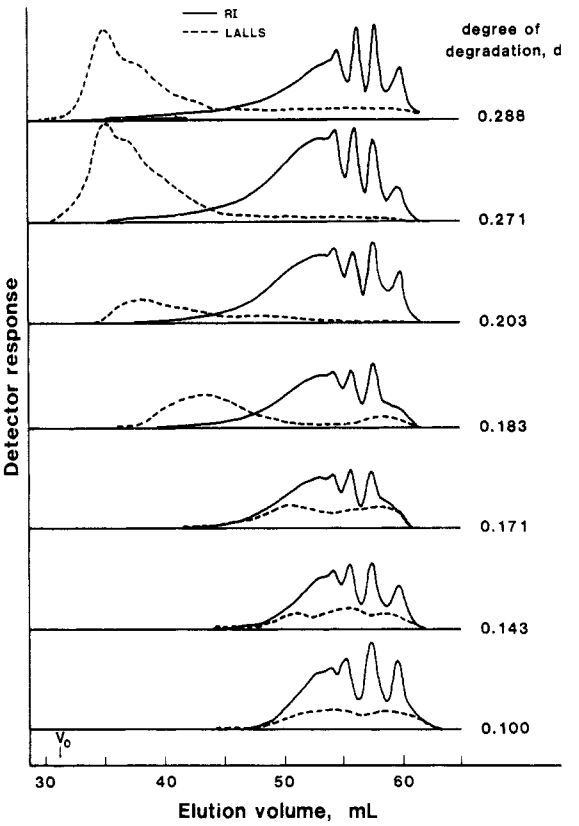

Figure 2. GPC/LALLS combined outputs of successive BTA/HDG network degradation sols as obtained by degrading the gels swollen in THF (columns used, μ-Styragel (Waters) in the sequence 10^5–10^4–10^3–500–10^6–100 Å).

Accordingly, an experiment was designed to determine the validity of this argument. It was necessary to find a different swelling medium in which, on degradation, the detached species would remain in solution. Tetrahydrofuran (THF) proved to be a suitable solvent.

Network Degradation in THF. When THF was used as the swelling medium, and degradation was effected by adding an equal volume of MeONa in methanol, the sol precipitation effects were eliminated. The THF–methanol network supensions remained colorless and clear during all stages of degradation. Figure 2 shows the composite chromatograms from the GPC/LALLS photometer of seven representative degradation fractions isolated during these experiments. The prime feature of these chroma-

Table II
Degradation of BTA/HDG Networks Swollen in THF

	experimental values			calculated values			
degradation time, min	wt % sol isolated	$\bar{M}_w$,[a,b] g mol^{-1}	$\bar{M}_n$,[b] g mol^{-1}	$\bar{M}_w/\bar{M}_n$	W_S[c]	d[c]	$\bar{M}_w$,[d] g mol^{-1}
2.5	1.5	1400	1070	1.29	0.0197	0.100	893
2.0	2.9	1990	924	2.10	0.0318	0.117	1048
4.0	3.8	1940	1280	1.51	0.0412	0.127	1153
6.0	5.6	1940	970	2.00	0.0607	0.143	1347
7.0	7.1	1000	858	1.20	0.0762	0.153	1490
7.5	10.6	3100	1650	1.90	0.1123	0.171	1803
11.0	13.5	4800	1620	2.96	0.1434	0.183	2068
9.0	17.5	4200	2600	1.60	0.1851	0.196	2400
14.5	20.2	8900	6300	1.43	0.2116	0.203	2664
15.0	55.5	10000	6400	1.58	0.5823	0.260	8311
13.5	67.3	9230	6500	1.41	0.6996	0.271	12781
16.5	88.6	49500	8700	5.67	0.9242	0.288	59000

[a] For comparison the theoretical $\bar{M}_w$ values are also given at the same value of d. [b] As determined by GPC/LALLS; average of three runs. [c] Calculated as described in the Appendix. [d] Using eq 1 of ref 8; setting $M_{Af} = 294$, $M_{B_2} = 258$, $M_c = 32$, $f = 3$, $r = 1$.

tograms, as compared to those in Figure 1, is that the species distribution is now continuous. This had not been the case, however, in the distributions of the sols from the methanol experiments (Figure 1), where the high and the low molecular weight components had been distinctly separated, especially for the samples at $d = 0.216$, 0.260, and 0.276. The sol sample (of Figure 1) at $d = 0.135$ had a continuous distribution, and is the only one whose molecular weight showed partial quantitative correlation with the theory (Table I). At this early stage of degradation the sol precipitation effect was only minor, because the low molecular weight fragments were still soluble in methanol.

The continuous distributions of Figure 2, together with their relatively higher elution volumes (compared to those of Figure 1), signify that these samples are now of lower average molecular weights. The chromatograms of Figure 2 also show all the characteristics expected in a sol degradation sample. They fully conform with the interpretation of such chromatograms as had been proposed by Bolker, Rhodes and Lee.[22] In this set of experiments the position of the LALLS maximum response gradually moves to lower elution volumes as the degree of degradation becomes progressively larger. Near the degelation point ($d_c = 0.293$), i.e., at $d = 0.271$ and 0.288, the LALLS response becomes very pronounced over the flattest parts of the RI response, thus indicating the presence of a very small amount of material of high molecular weight. On comparing the RI responses of Figure 2 with those of postgel sol samples,[21] the similarities between them become apparent. The crucial point in this comparison is that very similar chromatograms are obtained for both polymerization and degradation samples. Maximum heterogeneity (in terms of species distribution) is clearly shown to occur at both the gelation and the degelation critical points.

The composite qualitative picture of Figure 3 helps to clarify the mirror-image nature of both gelation and degelation, with respect to the $\bar{M}_w$ functions (the point at $p = 1.0$, $d = 0.0$ represents a mental mirror). A sample from any point beyond the gel point (or any point along the gelation curves, for that matter) is expected to show a similar molecular weight distribution to that of its mirror image samples taken prior to the degelation point. This statement is well supported by the results of the present investigation. Thus, the sol sample isolated at $p = 0.726$ exhibited the molecular species distribution of Figure 3b,[21] while its mirror image in the degelation, $d = 1 - p = 1 - 0.726 = 0.274 \simeq 0.271$, showed the strikingly similar distribution of Figure 3c.

The heterogeneity of the samples obtained by degradation in THF, together with the continuity of their distributions and their similarities to the polymerization sols, suggests that the THF degradation experiments conform with the requirements of the gel degradation theory. Even more significantly, the results point toward the validity of the gel degradation theory.

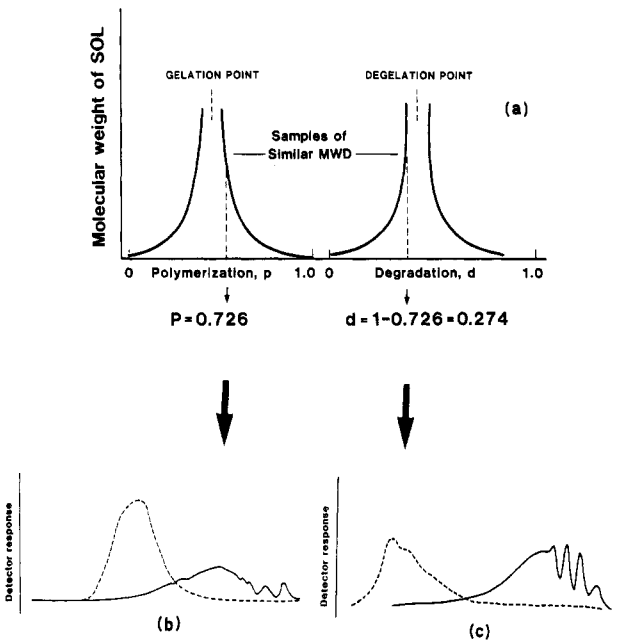

Figure 3. (a) The qualitative plot of $\bar{M}$ versus p and d for gelation and degradation, respectively, before and after their critical points. The dotted lines define two points, one beyond the gel point and one before the degelation point, at which the sol's molecular species distributions are expected by be similar. (b) GPC/LALLS output for BTA/DMG polymerization sol at $p = 0.726$.[21] (c) GPC/LALLS output for BTA/HDG degradation sol at $d = 0.271$.

The Quantitative Correlation. Confirmation of the validity was sought by correlation of experimental $\bar{M}_w$ values with their theoretical counterparts, with the results shown in Table II. The theoretical $\bar{M}_w$ values were derived by the application of eq 1 of ref 8. The degree of degradation, d, which is the equivalent of $1 - p$ (where p = extent of polymerization) has been calculated from the amount of soluble material isolated. The procedure for calculating d is given in the appendix.

For this set of samples, the dn/dc values had a mean value of 0.0499 mL g^{-1}, which was the value used in all calculations of $\bar{M}_w$. The second virial coefficient was taken to be 5×10^{-5} mol mL g^{-2} in accordance with published values for similar heavily branched polymers.[14,24-26] The agreement of experimental with theoretical $\bar{M}_w$ values

(third and last columns, respectively) is now nearly quantitative. The theoretical values lie so close to each other that the table should be examined as a whole; there is little to be gained by criticizing individual values and attempting to account for discrepancies.

The results in Table II are the first ever to show such a close correlation between experimental and theoretical $\bar{M}_w$ values obtained from model gel degradation experiments. Allowing for minor deviations, the trend of increasing $\bar{M}_w$ with increasing solubilization is clearly supported.

In addition, the increasing sample heterogeneity is apparent from the $\bar{M}_w/\bar{M}_n$ ratios, which assume their low and high values at the extreme ends of the process. All the samples in between show intermediary values, although they do not exactly conform to the expected trend. Near the degelation point, and at $d = 0.288$, the agreement between theory and experiment is particularly remarkable if one considers the errors in recursively calculating d and W_S from actual sol yields. The exponential nature of the curve in this region further strengthens the idea that the correlation is quantitative.

In a test of the postgel equation used here, as applied to polymerization beyond the gel point,[8] the observed deviations were explained in terms of diffusional considerations, especially at high conversions ($p \geq 0.75$).[20] It seemed likely that the original theoretical assumption of uniform functional group accessibility did not hold throughout the polymerization, because of the rigidity of the network at high extents of reaction.[20] This same equation however, when tested with experimental $\bar{M}_w$ values for the degradation prior to the degelation point, showed an almost quantitative fit. The improvement in correlation with experimental $\bar{M}_w$ values implies that the experimental simulation of random network degradation was more successful than the simulation of random network formation. Random bond cleavage is really determined by the degree of network swelling and is much easier to optimize experimentally in degradation than in simulating random bond formation in a dense polymeric network.

The Kinetics of Network Degradation. Another feature of the gel degradation theory is that it predicts accelerated degradation rates as one approaches the degelation point. This is because as degradation proceeds, a smaller number of bonds needs to be cleaved to free larger fragments. The detachment of larger fragments would thus amount to the formation of larger quantities of sol as degradation progresses. A plot of soluble fraction, W_S, versus degradation time should thus show an exponentially increasing trend, as is indeed the case for the degradation of BTA/HDG networks in THF, as shown in Figure 4, plotted from the kinetic results in Table II. Despite the scatter of results near the degelation point, the agreement with the expected trend is clear.

The plot in Figure 5 represents a comparison of the present results with Gardner's kinetic model[19] for the degradation of a trifunctional polymer network formed by condensation. The W_S data of Table II have been transformed to W_g (fraction of undegraded gel) by the simple relation: $W_g = 1 - W_S$. The time data for the experiment were transformed into dimensionless time by taking total dissolution time for the experiment as being equal to 17.85 min (Figure 4, assuming linearity in the time versus W_S relation in the region very near the degelation point). A reasonable agreement between the model and our experimental data was obtained, with some scatter of the experimental results. Gardner gave two plausible explanations for the scatter that he obtained. He considered the effect that intramolecular cross-links would have on the process. A certain degree of intramolecular cross-linking is actually unavoidable in forming any network. Such internal inconsistencies of networks have been held responsible for a variety of other discrepancies observed during gelation.[27,28]

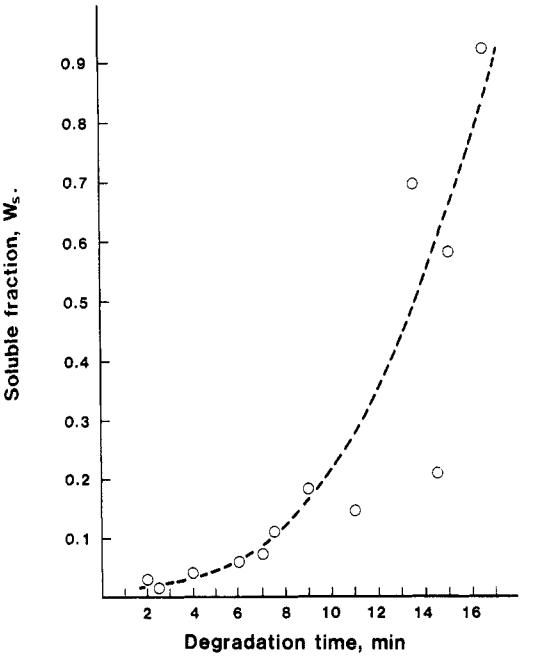

Figure 4. Degradation kinetics of BTA/HDG networks swollen in THF.

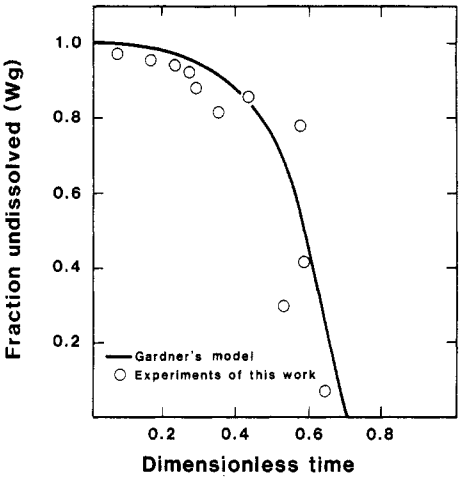

Figure 5. Plot of Gardner's kinetic model and the correlation observed for the degradation of BTA/HDG networks in the THF degradation experiments.

According to Gardner, the presence of intramolecular cross-links would accelerate sol formation as degradation approaches the critical point. The combination of 1,3,5-benzenetriacetic acid (BTA) with 1,10-decanediol (DMG) has been found to closely obey the random f-functional model proposed by Flory[28] with a minimum of cyclization.[29] Thus the networks used in the present experiments have been chosen so as to obey, as closely as possible, the ideal picture required by the gelation theory. The degree of cyclization in BTA/DMG networks has been determined to be less than 1%.[30] The degree of internal cyclization would be more pronounced in the networks of the type that Gardner examined.[19,31,32]. The effects of such network irregularities are thus expected to be minimal in the present results.

The second source of error that Gardner discussed was that of sol retention within the gel, early in the degradation process. The retained species would be released later in the process, close to degradation, as the gel loosens up. This phenomenon would have an accelerating effect on the observed kinetics at its later stages and a decelerating effect at its early stages. The present experimental results, however, show some errors in the opposite direction. The experimental procedure for degradation was carefully designed in this work to exclude, as much as possible, such sol retention effects. The weight of sol was an important quantity because it was used to calculate d, W_S, and theoretical $\bar{M}_w$ values. Thus every precaution necessary was taken so as to assure its accuracy.

Concluding Remarks

The degradation of BTA/HDG networks swollen in pure methanol only qualitatively accords with the gel degradation theory, because of sol precipitation during the reaction. The use of THF, however, as the swelling medium for the degradation reaction gave chromatograms showing highly skewed distributions for the molecular species that accorded with the interpretation that Bolker, Rhodes, and Lee[22] had given to the chromatograms of lignin samples. This series of degradation experiments produced sol samples which were qualitatively identical with gelation samples isolated after the gel point.

For the first time, a quantitative correlation of $\bar{M}_w$ values of the sol samples with their theoretical counterparts was observed. The trend of increasing molecular weight with increasing network solubilization was clearly supported by the results.

Kinetically, the process accords with the predictions of the gel degradation theory. Gardner's kinetic model[19] was found to correlate nearly quantitatively with the present results.

The degradation of BTA/HDG networks swollen in THF has given qualitative and quantitative agreement with the gel degradation theory. The results support the concept proposed; i.e., random network degradation follows the statistics of its formation. This observation justifies the assumption of reversibility of gelation originally proposed, in the context of wood delignification, by Szabo and Goring[10] in 1968.

Appendix

Procedure for Determining the Degree of Degradation, d, in BTA/HDG Networks. The conversion parameter, p, required to characterize the sol samples beyond the gel point could easily be measured by accounting for the amount of water liberated during the condensation reaction.[8,13,20] To obtain values for the extent of degradation, however, is more complex. The following represents a method for calculating d from the weight of degradation sol, adapted for the case of BTA/HDG networks.

In general, each ester bond cleavage reaction by sodium methoxide in the presence of a large excess of methanol is expected to consume some of the methanol by forming methyl ester end groups. By calculating, therefore, the amount of methanol consumed, one can determine the extent of degradation. The extent of degradation is then the weight of methanol consumed at a particular reaction stage divided by the theoretical weight of methanol consumed if degradation is complete.

Assume that one starts the degradation with 1.00 g of BTA/HDG network. Then this amount of network should contain 0.6060 g (2.344×10^{-3} mol) of HDG and 0.3939 g (1.563×10^{-3} mol) of BTA, which are 3 mol equiv of HDG and 2 mol equiv of BTA. One mole equivalent therefore equals 7.814×10^{-4} mol.

On fully degrading 1.00 g of network, 3 mol equiv of HDG should be formed (i.e., 0.6060 g) and 2 mol equiv of trimethyl benzene-1,3,5-triacetate (i.e., 0.4594 g). The two total 1.0654 g. Once again, at complete degradation, $6 \times 7.814 \times 10^{-4} = 4.688 \times 10^{-3}$ mol of bonds would have formed, this time consuming 4.688×10^{-3} mol of methanol or 0.1500 g. Berry[14] has derived the following relation between sol fraction (W_S), measured weight of sol ($W_{t\,sol}$), and extent of reaction in gel formation p, which when adapted to the BTA/HDG case is as follows:

$$W_S = W_{t\,sol}/(1.0654 - 0.1500p) \qquad (A.1)$$

or

$$W_{t\,sol} = 1.0654(W_S) - 0.1500p(W_S) \qquad (A.2)$$

The next step is to produce an array of W_s versus p theoretical values for the BTA/HDG degradation. This is done by solving eq 1 of ref 13 when setting the following variables: $M_{B_2} = 258$; $M_{Af} = 294$ (trimethyl benzene-1,3,5-triacetate); $M_c = 32$; $f = 3$; $r = 1$.

If the weight of degradation sol ($W_{t\,sol}$) was y g, then one has to enter a range of p and W_S theoretical values (produced from eq 1 of ref 13) into eq A.2 so that they will produce the value of y. By this iterative calculation, W_S and p can be fixed from the experimentally determined weight of sol. Finally, d can be found by simply subtracting the experimentally determined p value from unity.

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Surfactant-Free Emulsion Polymerizations: Predictions of the Coagulative Nucleation Theory

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ABSTRACT: Equations are set down for the formation of latex particles in emulsion polymerization systems in the absence of added emulsifier. The model describes the formation of colloidally unstable precursor particles through homogeneous nucleation, followed by their coagulation and propagational growth to form colloidally stable latex particles. Coagulation rates are obtained through DLVO theory and its modifications, with due allowance for the partial attraction that occurs in the coagulation between particles with different radii. Calculations show good agreement with the experimental data of Ottewill and co-workers for the variation of particle number density with initiator concentration and ionic strength.

Introduction

The mechanisms whereby polymer latex particles are formed in heterogeneous polymerization systems, both in the presence and absence of added surfactant, remain a matter for active investigation. At least three theories have been proposed to account for particle nucleation in heterophase polymerizations: the entry of free radicals into micelles,[1,2] homogeneous nucleation resulting from the precipitation of growing oligomers,[3-7] and the coagulative nucleation of precursor particles (subsequent to their formation by homogeneous nucleation).[4,8-12] The results of recent experimental determinations[12] of the time evolution and the size distributions of the latex particles formed in a conventional styrene emulsion polymerization appear to be in qualitative and quantitative conflict with the predictions of any single-step nucleation mechanism, including both micellar entry and simple homogeneous nucleation. These results are, however, in conformity with the predictions of the multistep nucleation mechanism postulated to be operative in the coagulative nucleation theory.[12] This theory is also consistent with the observation of periodic nucleation phenomena (Liesegang rings) in certain polymerizing systems.[13]

It has long been known that stable latex particles can also be generated in emulsifier-free systems, even with monomers such as styrene that are comparatively insoluble in water, provided that the initiator decomposition gives rise to charged primary free radicals. In such systems, the possibility of particle nucleation occurring by a micellar entry mechanism is virtually precluded. Although the micellization of the oligomeric surfactant molecules generated in situ in these systems has been postulated,[14] there is no experimental evidence even to hint at its occurrence. In these surfactant-free systems, coagulative nucleation appears to be significant in particle formation, as Ottewill and co-workers were the first to highlight.[9,10] These workers determined experimentally the effects of varying the ionic strength and the initiator concentration on the mean size of the latex particles formed. Their results were qualitatively in accord with the expectations of a coagulative nucleation mechanism.

A primitive theoretical treatment of coagulative nucleation has been presented previously.[12] It is worthwhile to examine the application of the model to systems in which there is no added surfactant. The precise experimental results of Ottewill and co-workers[10] for persulfate-initiated styrene systems provide a benchmark against which the quantitative predictions of the theory can be compared. The current paper gives a considerable development of the theory presented earlier,[12] as well as correcting some errors therein.

In coagulative nucleation, the basic mechanistic assumption is that the coagulation of "precursor" particles is involved in the formation of mature latex particles. These precursors are small (say, less than 5 nm in radius) and differ from true latex particles in two important respects. First, precursors are colloidally unstable. Second, precursor particles imbibe only relatively small amounts of monomer when compared with mature latex particles; thus, while growth occurs both by aggregation and propagation, the former must be important for smaller precursors. Both of these properties of precursors arise from the high curvature of their surfaces. Each precursor particle is composed of one or more primary precursor particles, the latter being formed by the propagational events that primary free radicals undergo in the aqueous phase after being generated by initiator decomposition. The particular character of the primary precursors is presumed to arise from oligomeric species whose chain lengths exceed the critical degree of polymerization required for solubility in the aqueous phase, i.e., homogeneous nucleation.

Coagulative Nucleation Theory

The coagulative nucleation theory calculates the rate of particle formation from (i) the rate of homogeneous nucleation and formation of primary precursors, based on the Hansen-Ugelstad-Fitch-Tsai (HUFT) theory;[7] (ii) the kinetics of coagulation among precursor particles, using the Smoluchowski-Müller-Fuchs theory, with the coagulation rate coefficients being calculated employing DLVO theory,[15] modified as required for heterocoagulation; and (iii) propagational growth.

Let Y_i be the number concentration of precursor particles with swollen volume $V_i = iV_p$, where V_p is the volume of a newly formed primary precursor particle. The pop-

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