Anionic Copolymerization of Styrene with *p*-Divinylbenzene

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ABSTRACT: The anionic copolymerization of styrene with *p*-divinylbenzene to form a gel exhibits simpler kinetic features than the comparable radical reaction. The growth in molecular weight of the basic polymer chain throughout the reaction causes the gel point to be delayed over that of the radical reaction where high polymer is formed from the start. In the reaction three types of vinyl groups may be described, and from them are formed three types of carbanion to propagate the reaction. Of the nine possible reactions between these species, the rate constants of six of them have been determined experimentally, and estimates of the others made. Although all three active anions show similar reactivities, the rate constants of reaction with *p*-divinylbenzene are tenfold greater than the others. From these rate constants it is possible to calculate the theoretical gel point, and this is found to differ considerably from the observed gel point. The difference is attributed to an abnormal occurrence of intramolecular cross-linking, caused by the nonuniform distribution of cross-linking units in the reaction solution.

Most studies of cross-linking and gelling in addition copolymerization of a monovinyl and a divinyl monomer have involved only radical or cationic processes. Living anionic polymerizations offer some attractive theoretical advantages in that very often a more thorough kinetic investigation can be made of systems in the absence of termination and transfer reactions, which may allow more insight into these rather imperfectly understood processes.

Flory's theory of gelation[1b] predicts that gelling will occur in an addition polymerization when one cross-link per two polymer molecules has formed. This point is delayed from the statistically expected time by the apparent preferential formation of intramolecular links or cyclization instead of the required intermolecular cross-links.[2,3] This effect is more pronounced in dilute solution polymerizations and in sufficiently dilute solutions no gelling at all occurs.[4] In radical polymerization the gel point is predicted to be at low conversions, because of the formation from the start of the reaction of high molecular weight material containing side chain vinyl groups available for cross-linking. Ignoring cyclization, this point, according to Flory, is given by the equation

$$P_c = 1/\rho_0 \bar{y}_w$$

for the case where all the vinyl groups have equal reactivity, P_c is the extent of reaction at the gel point, ρ_0 is the original fraction of vinyl groups on the difunctional monomer, and $\bar{y}_w$ the weight average degree of polymerization of the primary chains. Anionic living polymerizations,[5] where all chains are initiated at the start of the reaction and grow simultaneously, will require the modification that at the gel point $\bar{y}_w = \bar{y}_f P_c$ (where $\bar{y}_f = M_0/C_0$ is the ratio of initial monomer concentration over the growing chain concentration, or the final expected degree of polymerization of the primary chain). Then $P_c = 1/\rho_0^{1/2} y_f^{1/2}$, and for comparable anticipated final molecular weights the gel point occurs later in the anionic system than in the radical. The system found open to experimental investigation does not unfortunately satisfy the condition of equal activity of all the vinyl groups, but this complication is surmountable.

Previous attempts to measure detailed kinetics of anionic copolymerization systems have succeeded because of the facility with which concentration of the various active centers may be determined by their uv absorption.[6] Similar methods are applicable to the system styrene–*p*-divinylbenzene (*p*-DVB) because of the markedly different absorption peak of a polymer chain end with an anion formed from a *p*-DVB molecule, from that of the standard polystyryl anion. In the copolymerization it is possible to define three types of reactive chain ends, and three types of active vinyl groups, and hence there are nine possible reactions. Six of the rates have been measured, and from them reasonable estimates of the other three are possible.

The anions of the three active chain ends and the vinyl groups from which they are derived are shown in Figure 1. These anions are formed by anionic attack on the vinyl group of styrene, the first to be polymerized vinyl group of *p*-DVB, and the pendant double bond left when *p*-DVB is incorporated into the chain.

To avoid any difficulties with initiation the reactions were preinitiated with *sec*-butyllithium and styrene in benzene solution to give a short chain monofunctional polystyryllithium. The solvent chosen was benzene containing 2% tetrahydrofuran, a low dielectric constant mixture where the reactive chain ends are solvated ion pairs with uncomplicated kinetic behavior.[7] Polystyryllithium **1** has an absorption maximum at 335 mμ. When **1** is allowed to react with *p*-DVB, whose longest wavelength uv absorption band is at 316 mμ, there appears a new absorption band at 420 mμ[8] and the original polystyryllithium band at 335 mμ decreases. The band at 420 mμ is attributed to **2** formed by reaction at one of the vinyl groups of *p*-DVB. If there is an excess of *p*-DVB the new band stays while the absorption at 316

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mμ decreases, but when the *p*-DVB nears exhaustion the peak at 420 mμ begins to decrease and is replaced by another near 340 mμ as the new chain end begins to attack the pendant double bonds along the chain and forms **3**. When all the *p*-DVB has gone the absorption of the pendant vinyl groups **3′** at 296 mμ may be seen corresponding to the absorption of styrene at 292 mμ.

The reaction of polystyryllithium with styrene is the normal propagation step in the lithium alkyl initiated polymerization and has been measured before. The reaction of **1** with *p*-DVB to form **2** can be followed, in the absence of styrene, by the growth of the uv absorption of **2** at 420 mμ in the reaction of normal polystyryllithium with *p*-DVB. This reaction is rather fast for the methods used. The reaction of **2** with *p*-DVB can then be followed by recording the loss of the absorption at 316 mμ of the excess *p*-DVB or of a further addition of *p*-DVB. When all the *p*-DVB has been consumed, the rate of reaction of **2** with styrene may be measured by the drop in the absorption at 420 mμ if a sufficient excess of styrene is added to swamp the reaction of **2** with the pendant vinyl groups, **3′**. As all these reactions are part of a series of consecutive reactions; only the early parts of the reaction are valid for rate measurements.

To determine the rate of reaction of **1** with the pendant double bonds, 3′, in an intermolecular reaction (the primary cross-linking reaction), it is possible to treat **1**, prepared from butyllithium and styrene, with a solution of a copolymer of styrene and *p*-divinylbenzene which has been prepared separately in a reaction which has not been allowed to proceed past the point where appreciable reaction at the second vinyl group would occur. The reaction of **1** with **3′** is followed by the fall in the absorption at 296 mμ associated with these double bonds. The initial rate should be the required rate. The absorption peak of the resultant anion, **3**, is close to that of the original polystyryllithium and is not suitable for following the reaction. If there is a large excess of **3′** the later stages of the reactions, when all the initial **1** has been consumed, are a measure of the rate of reaction of **3** with **3′**.

Experimental Section

The purifications of the solvents and styrene have been described before.[6] *p*-DVB was separated from the Dow commercial mixture of divinylbenzenes by means of its cuprous chloride complex, as described by Rubinstein, *et al.*[8] The treatment was repeated to give a product better than 95% pure which could be crystallized from methanol to 99.8% purity. This was fractionally distilled under vacuum to free it from methanol. The major impurity was *m*-DVB.

The walls of the all-glass, sealed, reaction vessels were purged as described before,[6] and all manipulations were made under vacuum. The reagents were in fragile bulbs which were broken with glass-encased magnetic bars. All reactions were followed by uv spectrophotometry. The initiating polystyryllithium was prepared from distilled *sec*-butyllithium (Foote Mineral Co.) and styrene in benzene solution in a vacuum apparatus, and then diluted into many fragile bulbs which were sealed off. The *p*-DVB was similarly diluted after an initial drying over calcium hydride, and the bulbs were stored in a freezer.

Because of the rapidity of the reaction of **1** with *p*-DVB, the reaction vessel had two volume graduated arms each holding an optical cell. Solutions of the two reactants were made spearately in the two arms and their concentrations measured. The solutions were mixed by inverting the apparatus, and the reaction was followed in one of the optical cells. Some slow destruction of the *p*-DVB$^-$ chain end occurred at the low concentration used, but whether this was with the THF in the solvent or with residual impurities is uncertain. It did not interfere with the determination of the initial rates.

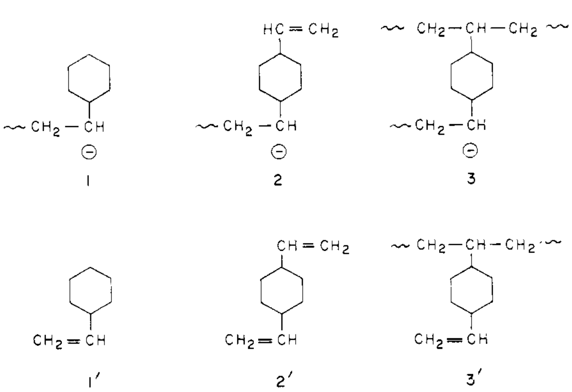

Figure 1. Structures of the vinyl groups present in the reaction, and the anions derived from them.

The polymer containing the pendant vinyl groups on the backbone, used to measure the reaction rates of these groups with the active chain ends, was prepared in 10% benzene solution from 1 g of *p*-DVB and 10 g of styrene in the presence of a little THF to promote the initiation reaction with butyllithium. The reaction was killed with methanol after 1 min and the yield was 2 g. At this point most of the *p*-DVB was incorporated into the chain, but because the first vinyl group reacts very much faster than the remaining group, little reaction at the second vinyl group should have occurred. The products molecular weight was 6000 as expected, and from its uv spectrum the polymer had about one pendant vinyl group per two chain units, assuming the extinction coefficient at 296 mμ of the vinyl group is similar to that of styrene at 292 mμ. During the reaction of this polymer with polystyryllithium some destruction of the chain ends occurred ($\sim 2 \times 10^{-5}$ *M*), presumably caused by impurities present in the difficult-to-purify polymer. The concentration of double bonds in these experiments was, except for one run, over ten times that of the living ends. The initial rate of disappearance of double bonds was taken to be that of the intermolecular crosslinking reaction, **1** + **3′**; the reaction rate at 20% reaction was assumed to be primarily that of the intramolecular reaction of these bonds with the *para*-chain-substituted polystyryllithium, **3** + **3′**, as no gel formed. The assumption is made that the rate constants for the equivalent intermolecular and intramolecular reactions would be the same provided the reacting groups involved in the intramolecular reactions are sufficiently widely separated on the chain that steric factors do not come into play, and also that the reactions are slow compared with chain motions. Both these conditions are met in these experiments, unlike radical polymerizations where Walling[2] considered the reaction to be fast. The reaction rates were taken from a first-order plot of the decrease in optical density at 296 mμ, where these double bonds absorb; in this way the uncertainty in assuming their extinction coefficient was the same as styrene was avoided. Moreover these first-order plots avoid the necessity of knowing the effcetive concentration which may differ from the formal concentration, and the true rate constant is found for both inter- or intramolecular reactions. The rate curves were slightly curved at the start because the initial intermolecular reaction (**1**, **3′**) was somewhat faster than the intramolecular one (**3**, **3′**).

TABLE I
RATE CONSTANTS IN THE COPOLYMERIZATION OF STYRENE AND *p*-DVB

Chain end[a]	Concn range × 10^5	Vinyl group[a]	Concn range × 10^5	Rate constant, mol/l. sec	Mean dev
1		**1′**		1.16	
1	4.7–21	**3′**	140–250	0.91	0.09
2	1.6–41	**1′**	1290–2460	1.12	0.08
3	2.7–20	**3′**	1030–1970	0.74	0.04
1	2.5–53	**2′**	5.5–208	12.3	1.2
2	3.6–19	**2′**	10–100	11.2	0.2

[a] The chain ends and vinyl groups are those designated in Figure 1.

Results and Discussion

The rate constants of five of the basic copolymerization reactions were measured over a range of concentrations, and no deviations from kinetics first order in both reactants were found, when only the initial stages of the reactions were studied. The consecutive nature of these reactions made it impossible to analyze complete reaction curves, not only because of the complexity of the reaction process, but because it was not always possible to isolate the required spectral change except at the start of the reaction. One other rate, the rate of the homopolymerization of styrene under these conditions, was calculated from available data,[7] and checked with one run only.

The rate constants are given in Table I and fall into two groups. The first group contains the reaction of all three types of active center with the single double bonds of styrene or the pendant chain double bonds, with a value close to 1 ml^{-1} sec^{-1} for the rate constant. The second group includes the reactions with *p*-DVB itself, containing the two conjugated double bonds, and has a rate constant a little over 10 ml^{-1} sec^{-1}. Thus it appears that the reactivity of the double bond is greatly enhanced by the vinyl group in the *para* position, and only affected in a minor way by the *para*-chain substituent. But neither a *para*-vinyl or a *para*-chain substituent on the benzyl-type anion affects much the activity of the chain end ion pair. Although the *para*-chain substituent might only be expected to have a minor effect, the small effect of the *para*-vinyl substituent on the reactivity of the ion pair is surprising. The vinyl substituent could be expected to withdraw some of the charge from the α-carbon atom and reduce its reactivity; this may be offset by the consequent loosening of the C$^-$–Li$^+$ bond and greater ease of inserting the next vinyl group. The product $r_1r_2 = 0.94$ for the pair styrene–*p*-DVB and exhibits close to ideal copolymerization behavior.

Estimates of the remaining three rate constants may be made. The reaction rate constant for **2** + **3′** is estimated to be near 0.8 ml^{-1} sec^{-1}, similar to the constant of the other two anions. But as neither species is likely to have a high concentration, the reaction is not likely to be important. The reaction of **3** + **2′** probably has a constant close to 10 ml^{-1} sec^{-1}, and again is not likely to be important. The third unmeasured reaction, **3** + **1′**, will occur nearly as frequently as the reaction **1** + **3′** and probably has a constant close to 1 ml^{-1} sec^{-1}.

Using all these nine measured and calculated rate constants it is theoretically possible to calculate the path of the whole polymerization. Under normal copolymerization conditions required to form a cross-linked structure, and using a small amount of difunctional monomer, the anionic reaction scheme may be approximated by a scheme involving only three rate constants, those of the polystyryllithium itself with the three types of double bonds. This is because the large excess of styrene molecules over all the other types of double bond results in the rapid regeneration of polystyryllithium from the other types of active chain end when they form. If the rate constants for the addition to another type of double bond had been very much greater than that of styrene it is possible that the chain end corresponding to that species could have a concentration comparable with polystyryllithium. The tenfold greater rate constants for *p*-DVB is insufficient to make ion **2** an important species unless the ratio of styrene to DVB is much less that 100. Even so the similarity of activity of these three types of chain end would make it not too important in the reaction scheme.

Hence from the beginning of the reaction the polystyryllithium will react with both styrene and *p*-DVB and they will be consumed in a normal first-order fashion at their respective rate constants. All the polymer chains will thus grow, but for each *p*-DVB incorporated along the chain a pendant double bond will appear along the chain. The concentration of these bonds will at first grow, but as it does so the rate of their reaction with polystyryllithium to form cross-links will increase until it equals their rate of formation, and then their concentration will decline as the *p*-DVB is consumed, in the fashion of the intermediate in two consecutive reactions. As the rate of reaction for *p*-DVB is about ten times that of styrene, most of the *p*-DVB is incorporated while only 10% or so of the styrene is consumed, and most of the pendant double bonds occur in the first 10–20% of the chain. Then as the rate constant for the consumption of styrene is much the same as for the reaction with these pendant double bonds, the chain ends will react on the average at fairly regular intervals during the chain growth with these bonds to form the cross-links. Figure 2 illustrates the course of the reaction, showing the rapid consumption of the *p*-DVB compared with styrene, the rapid buildup and slow fall of pendant double bond concentration, and the rise in cross-links.

The above treatment does not distinguish between intermolecular cross-links and intramolecular cross-links, and it is only the former which contribute to gel formation. If all pendant double bonds had equal opportunity to react with the chain end, as would be ex-

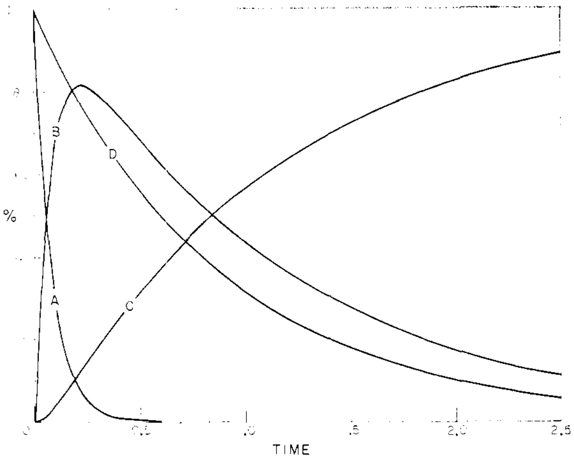

Figure 2. Reaction curves in copolymerization of styrene with *p*-DVB: curve A, disappearance of *p*-DVB plotted as per cent remaining; curve B, appearance and disappearance of pendant double, bonds plotted as percentage of *p*-DVB originally present; curve C, appearance of cross-links, internal and external; curve D, disappearance of styrene, plotted as per cent remaining The time scale is in units of *t*[PsLi], sec.

pected if the reaction was slow, because the total number of pendant double bonds vastly outweighs those attached to any given chain, the number of internal cross-links would be negligible and the gel point would be the point where one cross-link per two chains has formed. This point would occur when the percentage of cross-links is 100[PsLi]/2[DVB] of the total theoretical number, the theoretical maximum number of possible cross-links per chain being [DVB]/[PsLi]. In Table II are shown the gel points as calculated above, and the observed gel points for two copolymerizations. The actual gel point occurs very much later than this simple calculation would predict. Evidently there is considerable internal cross-linking, and the probability of internal reactions must be higher than that of the external which could be due to the peculiar conformation of polymers in solution. The average concentration of external pendant double bonds seen by any given active chain end is the formal concentration. But the internal bonds attached to its chain will in fact have an effective concentration greater than the formal by virtue of the restriction that they are contained in the volume occupied by the polymer chain, and because the reaction is slow the chains will always have time to assume their statistical shape.

In dilute solution only a small part of the total volume is occupied by the polymer molecules in their random coil shape. The pendant vinyl groups attached to the chain will appear, before cross-linking, as small local concentrations each associated with one chain and one active chain end the average of which over the whole solution is the formal concentration. The ratio of the internal to the external cross-links could be expected to be the same as the ratio of the local concentration of vinyl groups in the volume occupied by the polymer molecule to the overall concentration. This ratio is approximated by the ratio of the mean concentration of the polymer in the volume it occupies in solution to that of the formal concentration. Assuming that the polymer takes its unperturbed dimensions, these ratios are near 15 and 5.5, respectively, for the first and second examples in Table II at the point in the reaction where half a cross-link has occurred per molecule. As benzene is a good solvent these ratios may be somewhat overestimated, but nevertheless there is a high probability that mostly intramolecular links will form. This neglects the further effect that the chain end is enclosed in the excluded volume occupied by the polymer chain which might have a depressing effect on the effective external pendant double bond concentration in the region of the active end. These considerations only concern the interchain reactions. Small molecules such as the two monomers are effectively part of the solvent and their effective concentration will always be their formal concentration,[3] unless some preferential absorption on the chain occurred.

TABLE II

CALCULATED AND EXPERIMENTAL GEL POINTS

[Styrene]$_0$, M	[*p*-DVB]$_0$, $M \times 10^{-3}$	[PsLi]$_0$, $M \times 10^{-5}$	Gel point, % Calcd	Gel point, % Obsd
0.374	1.60	8.21	8.5	77
0.714	1.12	8.37	10.5	47

At the point where gelling occurred in the above two reactions the unperturbed dimensions of the polymers would have been about twice the volume available and considerable interpenetrations of polymer molecules must have occurred, offset somewhat by the reduction in dimensions of the polymer molecule in solution as it gained internal cross-links. Evidently the more concentrated solutions, where the volume unoccupied by polymer molecules is less, should approximate more to the simple kinetic theory. Conversely if the ratio of the local concentration of pendant vinyl groups to overall formal concentration sufficiently exceeds the number of cross-links per chain, the solution may not gel, as in fact is found in more dilute solutions.

It is unfortunately not possible by these experimental methods to follow the individual reactions throughout an actual copolymerization because of the mutual interference of the absorption bands of the vinyl groups. The main carbanion absorption was, however, that of the polystyryllithium in accord with the above predictions. In reactions in which gelation occurred it was observable that no change in rate of consumption of styrene occurred as the solution went through the gel point. The reaction did appear to slow down toward the very end, but measurements in such a stiff gel might not be reliable. In reactions in more dilute solution which did not gel, it was observed that some pendant double bonds remained unreacted when all the styrene had gone. Their immobilization within the cross-linked lattice evidently reduced their ability to react, probably not an important effect when the chain end is mobile as it grows through addition of styrene, but when the styrene has gone the chain end would soon become immobilized as well.