The Kinetics of Two-Phase Bulk Polymerization.
I. Monomer and Initiator Distribution

W. A. LUDWICO and S. L. ROSEN, *Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213*

Synopsis

Rubber-reinforced thermoplastics are produced commercially by dissolving a rubber in the monomer of a glassy polymer and commencing polymerization with a free-radical initiator. Beyond a few per cent conversion, the incompatibility of the two polymers causes a phase separation, with each phase containing one nearly pure polymer. Subsequent polymerization occurs in each phase. The heterogeneous nature of the reaction can influence both the kinetics of the reaction and the amount of grafting in the product. The fact that only monomer which polymerizes in the rubber phase can possibly graft establishes an upper limit to the amount of grafting and hence influences the mechanical properties of the product. It is shown theoretically how unequal partitioning of monomer and initiator between the phases can influence the extent of grafting, and can also explain the kinetic rate reductions which have been observed in such systems. The distributions of monomer and benzoyl peroxide and azobisisobutyronitrile initiators between the phases have been determined experimentally for a styrene–polystyrene–polybutadiene system. They cannot account for the rate reduction observed in such systems.

INTRODUCTION

Two-phase polymer systems have become important items of commerce over the past two decades. By combining two existing materials to form a composite with certain properties superior to those of either component, they provide a relatively inexpensive way of obtaining materials with new and useful properties. Two important examples are the high-impact polystyrenes and the ABS plastics. They are typical of systems in which dispersed rubber particles are used to toughen a normally brittle thermoplastic resin. These materials have been extensively reviewed.[1-3]

This work deals specifically with one of the common synthesis techniques used to produce such rubber-reinforced thermoplastics. Typically, the rubber is dissolved at a 5–20% level in the monomer of the glassy polymer and a free-radical initiator is added. The reaction can be followed on the phase diagram in Figure 1. This diagram is representative of nearly all polymer–polymer–common solvent systems. Despite the fact that each polymer alone is infinitely soluble in the solvent (in this case, the monomer of the glassy polymer), it takes very little of a second polymer to form a heterogeneous system, each layer containing nearly pure polymer. This incompatibility is a direct result of the extremely small entropies of solution for high-polymer pairs. The extent of the homogeneous region depends on the particular system, the temperature, and the
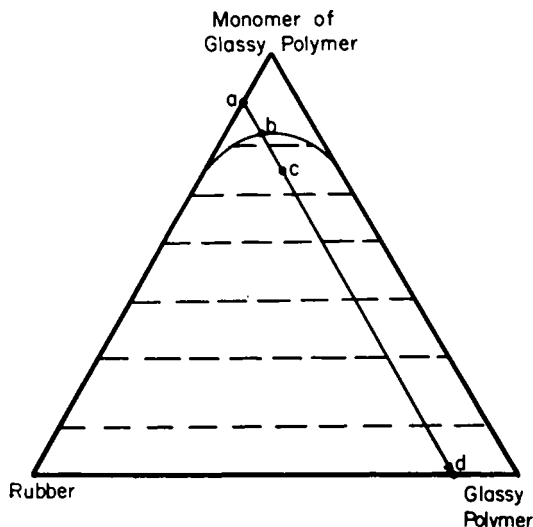
Fig. 1. Phase diagram for rubber–glassy polymer–monomer system. Point a, initial reaction mass; point b, phase boundary; point c, phase inversion; point d, complete conversion.

molecular weight of the polymers, lower molecular weights enhancing compatibility. Nevertheless, for polymers with molecular weights high enough to be of commercial interest, the initially homogeneous reaction mass (point a, Fig. 1) becomes a heterogeneous system at a few per cent conversion as the reaction vector reaches the phase boundary (point b, Fig. 1) on its path parallel to the monomer–glassy polymer axis. The formation of new surface area upon crossing the phase boundary requires energy; and if this energy is not available, it is conceivable that a supersaturated solution could persist beyond the phase boundary. But surface tensions in those systems are low, and the necessary energy is easily supplied by the agitators in commercial reactors.

If the reaction vector passes to the left of the plait point (as is the case in most systems of commercial interest), the rubber phase will initially be continuous. As the reaction proceeds, however, more and more glassy polymer is produced, and a phase inversion occurs (point c), leaving the rubber phase dispersed in a continuous glassy phase (with occasional, small, glassy inclusions trapped in the rubber particles as remnants of the preinversion state). The reaction is carried to completion (point d), giving the final product: 5–20% of micron-sized rubber particles dispersed in a continuous glassy matrix. It is possible to avoid phase inversion in quiescent systems. The product then consists of relatively large glassy globules with rubber in the interstices. This morphology does not give the desired mechanical properties in the product and is easily and routinely avoided by agitation. With even minimal agitation, the conversion at which phase inversion occurs is reproducible.[4]

One of the major reasons for producing rubber-reinforced thermoplastics in the manner outlined above (as opposed to a simple mechanical blending of the rubber and glass) is to promote the formation of graft copolymer—chains of glassy polymer growing from a rubber backbone. Thermodynamically, this graft copolymer would be expected to distribute itself at the rubber–glass

interface and enhance compatibility, much as a soap emulsifies droplets of oil in a continuous water phase. This graft copolymer is felt to have a very beneficial effect on the mechanical properties of the composite (e.g., 5). During the synthesis reaction, the major function of the graft seems to be to stabilize the so-called polymeric oil-in-oil emulsion (POO). Molau and Keskkulla[4] studied viscosity versus conversion in this type of reaction by simulating the reaction mass with mixtures of rubber, glassy polymer, and monomer stabilized with small amounts of rubber-glass graft copolymer. They observed a reversible (in terms of composition) sharp drop in viscosity at phase inversion, which did not depend on the amount of graft used. A viscosity drop at the same (simulated) conversion was observed without any graft at all, although the systems settled more rapidly (hours instead of days) upon standing without agitation.[6]

During the course of these reactions, monomer is converted to glassy polymer in two thermodynamically incompatible phases. The overall rate of reaction in the system will be the sum of the rates in each phase. The rates in each phase will in turn depend on how monomer and initiator are distributed between the phases. This work was undertaken to examine theoretically and experimentally the consequences of uneven distribution of monomer and initiator between the phases.

PREVIOUS KINETIC STUDIES

A number of kinetic studies of the initial, homogeneous regime (which only accounts for a few per cent of the total conversion in a commercial reaction) have been conducted. Scanlon[7] investigated the effects of dihydromyrcene (DHM; an isoprene dimer) on the polymerization of styrene, methyl methacrylate, methyl acrylate, and vinyl acetate. Although the molecular weights of the resulting polymers could be explained by a simple chain transfer mechanism, he observed a depression in polymerization rate caused by the DHM which could not be explained by a simple chain transfer mechanism. It should be noted that DHM may not be a good model for high molecular weight polyisoprene because of its much higher entropy of solution, i.e., solutions of DHM will more nearly approach true homogeneity than solutions of high molecular weight polyisoprene.

Merrett[8] investigated the polymerization of styrene and methyl methacrylate in the presence of a high molecular weight polyisoprene using benzoyl peroxide (BPO) and azobisisobutyronitrile (AZBN) initiators. He attempted separation of the product into rubber homopolymer, graft copolymer, and glassy homopolymer fractions by solution techniques. He found that a graft fraction was obtained with BPO but not with AZBN, but that the grafted chains were far shorter than the homopolymer chains, contrary to what would be expected from a simple chain transfer mechanism. This led him to postulate direct attack of the rubber chains by BPO radicals, but the number of radicals required to produce the experimentally determined number of grafting sites far exceeded the number of radicals available from the BPO.

Later studies by Allen, Merrett, and Scanlon[9] refuted many of the earlier results. Polymerization of methyl methacrylate in the presence of DHM using BPO and AZBN initiators fit a simple chain transfer mechanism, and no rate reductions were observed. Earlier observations of rate reduction were attributed to inhibitors in the DHM. With vinyl acetate monomer, they found that the

addition of 0.5 mole/l. DHM cut the rate by two orders of magnitude, regardless of initiator. To explain this, they proposed a "degradative chain transfer" mechanism, i.e., radicals produced by the attack of growing vinyl acetate chains on the chain transfer agent (DHM) are resonance stabilized to the point where they are slow to reinitiate polymerization of this monomer.

Allen and Merrett[10] repeated earlier experiments, polymerizing methyl methacrylate in the presence of high molecular weight polyisoprene with AZBN and BPO initiators, and again reached the conclusion that no graft was formed with AZBN initiator. A different separation procedure revealed that the grafted and free poly(methyl methacrylate) had the same chain lengths, in contrast to previous results. Rate reductions were observed with each initiator, eliminating simple chain transfer from consideration and raising the question as to why rate reduction should be observed with AZBN even in the absence of detectable grafting. Note that the Trommsdorff or gel effect would increase the rate of reaction, not reduce it.

Ayrey and Moore[11] used radioactively tagged initiators followed by separation of the reaction product to gain further insight into the reaction mechanism. Again, no simple mechanism could explain their results. Ide, Sasaki, and Deguchi[12] polymerized methyl methacrylate, styrene, and vinyl acetate in the presence of acrylic rubbers with BPO and AZBN. They separated their reaction products by solution techniques and claimed grafting for both BPO and AZBN initiators, although more with the former. They also observed rate reductions caused by the rubber, eliminating a simple chain transfer mechanism from consideration even though measured chain lengths agreed with the predictions of a chain transfer mechanism. Interestingly, this investigation may have carried kinetic measurements into the heterogeneous regime, although it is impossible to tell from the data in the paper. The authors present conversion-versus-time curves carried to about 96% conversion and label them "bulk" polymerization. However, their experimental procedure calls for the use of benzene, an inert solvent, in unspecified amounts. An inert solvent would delay phase separation, or even prevent it, if the total polymers concentration remained low enough. Such solvents are not generally used commercially, as they waste valuable reactor space. The fact that they "poured" their reaction products implies a rather large percentage of inert solvent, because a mixture of 90% methyl methacrylate and 10% rubber carried to 96% conversion will not pour, even at their reaction temperature of 75°C. In any case, further kinetic analyses were based only on rates at 10% conversion.

Kumar[13] polymerized styrene in the presence of several different molecular weight polybutadienes using AZBN and BPO initiators. He observed rate reductions which increased with the molecular weight of the polybutadiene and were greater for BPO than for AZBN. No plausible chemical mechanism could be found to explain his results adequately.

Kolesnikov and Khanukaeva[14] polymerized styrene in the presence of a styrene–butadiene copolymer rubber with BPO initiator up to conversions of 40%. Although they never mentioned the undoubtedly heterogeneous nature of their reactions, they observed rate reductions on the order of 100% at rubber concentrations approaching 10%.

In summary, no clear picture exists as yet of the mechanism of reaction in the initial, homogeneous reaction stage, and no quantitative model has been de-

veloped for it. Any data purporting to establish the extent of grafting by separation techniques must be viewed with skepticism, on both thermodynamic and experimental grounds. While this is most unfortunate from an intellectual standpoint, on practical grounds it is much less significant, because the homogeneous region is responsible for such a small portion of the total conversion in commercial practice.

THEORY

In the heterogeneous regime, each phase may be considered an independent reactor for the conversion of monomer to glassy polymer. Glassy homopolymer formed in the rubber phase diffuses to the glassy polymer phase, and any graft formed diffuses to the interface to stabilize the system. The overall rate of conversion of glassy monomer to polymer in the heterogeneous regime is given by

$$r_p = r_p'(1 - v'') + r_p''v'' \tag{1}$$

where a single prime denotes the glassy polymer phase, a double prime the rubber phase, and the v's are volume fraction. Under isothermal conditions,

$$r_p' = r_p' \, ([I]', [M]') \tag{2a}$$

$$r_p'' = r_p'' \, ([I]'', [M]'') \tag{2b}$$

where the overall initiator $[I]$ and monomer $[M]$ concentrations are related to those in each phase by

$$[I] = [I]' \, (1 - v'') + [I]'' \, v'' \tag{3a}$$

and

$$[M] = [M]' \, (1 - v'') + [M]'' \, v''. \tag{3b}$$

The partitioning of monomer and initiator may be represented by distribution coefficients

$$K_I = [I]''/[I]' \tag{4a}$$

$$K_M = [M]''/[M]' \tag{4b}$$

which, in general, will be functions of conversion. It might be argued that eqs. (4a) and (4b) are not necessarily applicable because of the possibility of diffusion limitations in a reacting system. Simple calculations show, however, that because of the very small dimensions of the discontinuities (microns) and the long initiator half-lives and times of monomer conversion (tens of hours) in typical systems, these reactions are not limited by diffusion between phases. For the same reason, variations in agitation (beyond that necessary to produce and maintain dispersion) and the occurrence of phase inversion should not influence the reaction rate.

To illustrate what could happen in the heterogeneous system, consider the case where the homogeneous reaction in each phase is described by the classical rate expression for free-radical polymerization[15]:

$$r_p = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [I]^{1/2} \, [M]. \tag{5}$$

TABLE I
y Versus v'' for Various K_I Values[a]

v''	$K_I = 1$	0.6	0.4	0.2	2	4	6	8
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
0.8	1.0	0.994	0.979	0.930	0.992	0.976	0.983	0.959
0.6	1.0	0.992	0.974	0.927	0.987	0.956	0.935	0.920
0.4	1.0	0.993	0.978	0.945	0.985	0.944	0.912	0.888
0.2	1.0	0.996	0.983	0.971	0.989	0.949	0.912	0.882
0.1	1.0	0.998	0.994	0.985	0.993	0.965	0.935	0.907

[a] $K_M = 1$.

It is assumed that the rate constants and initiator efficiencies are the same in each phase. Using eq. (5) for eqs. (2a) and (2b) and combining with eqs. (3) and (4) gives

$$r_p = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [I]^{1/2} [M] \left\{ \frac{(1 - v'') + K_M K_I^{1/2} v''}{[(1 - v'') + K_M v''] [(1 - v'') + K_I v'']^{1/2}} \right\} \quad (6)$$

Defining $y = r_p/r_{p0}$, the ratio of the overall rate in the heterogeneous system to the rate in a homogeneous system with the same overall monomer and initiator concentrations,

$$y = \frac{(1 - v'') + K_I^{1/2} K_M v''}{[(1 - v'') + K_M v''] [(1 - v'') + K_I v'']^{1/2}}. \quad (7)$$

If $K_I = 1$, eq. (7) reveals that $y = 1$ for all v'' and K_M, i.e., the presence of the rubber producing a second phase does not alter the overall rate at all. This merely reflects the first-order dependence of rate on monomer concentration in each phase. A more interesting result is obtained for the case $K_M = 1$, i.e., equal interaction of the monomer with each of the polymers. Under these conditions,

$$y = \frac{(1 - v'') + K_I^{1/2} v''}{[(1 - v'') + K_I v'']^{1/2}}. \quad (8)$$

Table I gives y versus v'' for various values of K_I (see also Fig. 5). A reduction in rate is always obtained. Interestingly enough, the reductions are similar in nature to those observed in kinetic investigations.

On further reflection, the rate reduction described above for the heterogeneous reaction regime due to unequal partitioning of initiator could turn out also to be the explanation for the rate reductions observed in the initial, homogeneous reaction regime. It is doubtful that any solution of a high molecular weight polymer in a low molecular weight solvent is truly homogeneous (whatever that means). In fact, theories of dilute polymer solutions model them as pseudo-heterogeneous systems—polymer molecules with associated "bound" solvent floating around in "free" solvent.[16] The size of these polymer-bound solvent domains is a couple of orders of magnitude smaller than the particles in the truly heterogeneous regime—several hundred angstroms versus a micron, or so. The usual way of defining the phase boundary is to observe the light scattered by the system as the reaction progresses. It is known that turbidity is a function of the difference in refractive index between phases and the particle size of the dispersed phase (increasing with each in the range of interest here).[17] At low conversions, the difference in refractive index can never be very great, since both phases

consist largely of the same unreacted monomer. It is entirely possible that the abrupt increase in turbidity associated with phase separation is a result of a rather sudden coalescence of the polymer-bound solvent domains into much larger (micron-sized) particles as more glassy polymer is generated, but without any abrupt change in composition, and therefore with the same sort of initiator partitioning existing before and after visible phase separation. This would imply that there is no discontinuity in rate as the reaction vector crosses the phase boundary. Indeed, Hawthorne could detect none, although his experiments were admittedly of low precision.[18] In summary, all the kinetic observations to date can be explained, at least qualitatively, on the basis of unequal initiator partitioning.

Not only will the distributions of initiator and monomer between phases in these heterogeneous reactions influence the rate of reaction, but they also affect the maximum extent of grafting which can be accomplished. It was pointed out in an earlier article[19] that only that monomer which is converted to polymer within the rubber phase can possible graft to the rubber. Monomer which polymerizes in the glassy polymer phase is never in contact with rubber, and so cannot graft to it. This establishes a physical upper limit to the extent of grafting, regardless of the chemical nature of the grafting reactions.

The differential amount of monomer converted to glassy polymer while in the rubber phase, df, is given by the product of the fraction of monomer converted in the rubber phase and the incremental conversion of monomer to polymer, dX:

$$df = \frac{r_p'' v''}{r_p'' v'' + r_p' v'} \, dX. \tag{9}$$

Inserting equations (4) and (5) gives

$$df = \frac{K_I^{1/2} K_M v''}{K_I^{1/2} K_M v'' + v'} \, dX. \tag{10}$$

Equation (10) illustrates that the maximum extent of grafting is enhanced if initiator and monomer favor the rubber phase (high K_I and K_M), and vice versa. If it is further assumed that the densities of all components of the reaction mass are the same (such that volume fractions are equal to mass fractions) and that the phases are at all times *equally* swollen by monomer, i.e., $K_M = 1$, eq. (10) reduces to

$$df = \frac{K_I^{1/2} v_{r0}}{K_I^{1/2} v_{r0} + v_g} \, dX \tag{11}$$

where v_{r0} = initial volume (or mass) of rubber, a constant; and v_g = volume (or mass) of glassy polymer.

The amount of glassy polymer present is, by definition, proportional to the conversion, i.e., $v_g = v_{m0} X$, so that

$$df = \left(\frac{K_I^{1/2} v_{r0}}{K_I^{1/2} v_{r0} + v_{m0} X} \right) dX \tag{12}$$

where v_{m0} = initial volume (or mass) of monomer, a constant. For a batch reactor, neglecting the initial homogeneous portion of the reaction and assuming that K_I is constant, eq. (12) integrates to

$$f = \frac{K_I^{1/2} v_{r0}}{v_{m0}} \ln \left[1 + \frac{v_{m0}}{K_I^{1/2} v_{r0}} X \right]. \tag{13}$$

The quantitative implications of eq. (13) have been discussed in great detail for the case where $K_I = 1$.[19] These earlier results can be generalized to include the case $K_I \neq 1$ by replacing the parameter v_{m0}/v_{r0} in the earlier work with $v_{m0}/K_I^{1/2}v_{r0}$.

These examples serve to illustrate how both the overall rate of the reaction and the maximum extent of grafting achieved are controlled by the details of how the reaction proceeds individually in each of the phases. It is recognized that some of the assumptions used in the preceding developments may not always be valid. For example, the Trommsdorff or gel effect (diffusion limitation of the termination reaction) may invalidate the assumption of classical kinetics, eq. (5), in one or both phases over certain conversion ranges. Nevertheless, the overall rate should be given by eq. (1), i.e., should be directly dependent on the rates in the individual phases and should therefore be a function of monomer and initiator distribution between the phases, as should the maximum possible extent of grafting through eq. (9).

EXPERIMENTAL

Two factors preclude the determination of initiator distributions in actual reacting systems. First, the reaction would continue, with the attendant increase in monomer conversion and decomposition of initiator during the separation of the phases. Second, formation of graft copolymer during the reaction can stabilize the two-phase system to an extent that separation becomes exceedingly difficult and time consuming, if not impossible.[4] As a result, initiator distributions were determined in simulated reaction systems: solutions of styrene monomer, polystyrene, and polybutadiene simulating a reactor charge of 5% polybutadiene in styrene at conversion levels of 5%, 10%, 15%, 20%, and 25%. Extremely high viscosities made determinations at higher conversions impossible. Experiments were performed at 25°C and 0°C, temperatures low enough so that no appreciable initiator decomposition (BPO 25°C half-life 8700 hr; AZBN 25°C half-life 3500 hr[20] or polymerization occurred in the time required to dissolve the initiator, reach equilibrium, and separate the phases.

Weighed portions of Firestone 35-NFA polybutadiene ($\bar{M}_v$ 320,000), Dow Styron 666 polystyrene ($\bar{M}_v$ 360,000) and styrene monomer (10 ppm MEHQ) were stirred magnetically for 48 hr to ensure complete dissolution, after which AZBN or BPO was added to a level of 3–6 g/l. (typical of commercial practice) in the simulated samples, and stirring continued for 3 hr. The resulting solutions were poured into calibrated centrifuge tubes and were maintained at 25°C or 0°C during phase separation in a Sorvall RC-2B centrifuge. Previous studies on samples without initiator had established the times necessary to reach a steady-state phase-volume ratio at each simulated conversion level. The times thus determined were doubled for the runs with initiator to insure complete separation. With the Sorvall SS-34 rotor at 17,000 rpm, separation times were from 1 to 3 hr, depending on (simulated) conversion level. The phase-volume ratios so obtained were reproducible to 1%, within the calibration precision of the centrifuge tubes.

Aliquots of the rubber and polystyrene phases were carefully removed from the centrifuge tube with a syringe. Because of the high viscosities, it was difficult to measure volumes accurately, so the amounts of each phase withdrawn for analysis were determined by weight. The densities at 25°C of the phases were

determined independently at each conversion level with pycnometers. Densities at 0°C were obtained from the 25°C data and the coefficient of thermal expansion of styrene. This procedure has been shown to be valid within 0.3% for similar systems.[21] Monomer distribution coefficients were obtained gravimetrically by drying aliquots of the separated phases to constant weight in a vacuum oven at 60°C.

Approximately 1 g of each phase and of the preseparation sample were analyzed for initiator content by the polarographic technique described by Dmitrieva and Bezuglyi.[22,23] The aliquot was delivered to a 50-cm³ volumetric flask by syringe and diluted with 10 cm³ of benzene. The polymer was precipitated by adding LiCl in methanol to the 50-cm³ mark. The LiCl acted as the supporting electrolyte. Final electrolyte concentration was $0.15M$ LiCl in 4:1 methanol: benzene for AZBN and $0.03M$ LiCl for BPO. After thorough shaking and 25 min for settling, the supernatant liquid was poured into a polarographic cell similar to the anhydrous type described by Lingane.[24] Nitrogen, presaturated with 4:1 methanol:benzene, was bubbled through the solution for 15 min prior to applying the voltage. Polarograms were obtained between -1.0 and -1.9 volts for AZBN and between -0.35 and -1.0 volts for BPO against a saturated calomel electrode. Both cell and reference electrode were submerged in a 25°C constant-temperature bath. Initiator concentrations were obtained from the polarograms and a linear calibration curve of wave height versus initiator concentration.

Independent checks using known initiator concentrations demonstrated that neither initiator was occluded by either of the precipitated polymers over the range of polymer concentrations investigated. Furthermore, there were no impurities in the polymers or monomer used which were detectable by the polarographic technique.

RESULTS AND DISCUSSION

Experimental initiator distribution coefficients for AZBN and BPO at 0° and 25°C are shown in Figures 2 and 3. In all cases, the material balances relating measured individual phase properties to overall properties, eq. (3a), agreed to within 2%.

Each initiator slightly favors the polystyrene phase ($K_I < 1$). Within experimental precision, K_I for BPO shows no significant variation with conversion, but
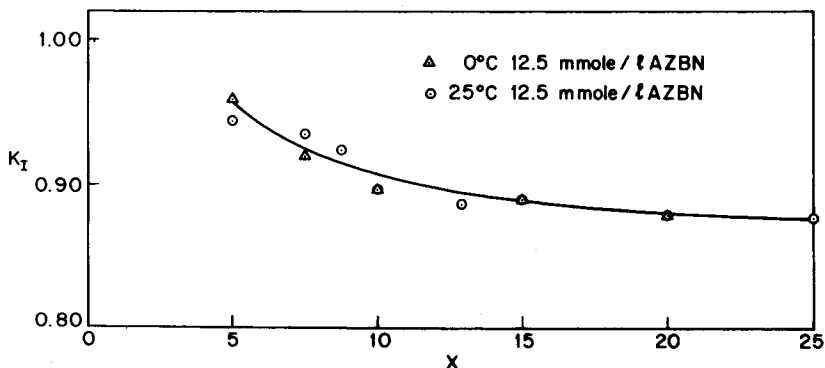

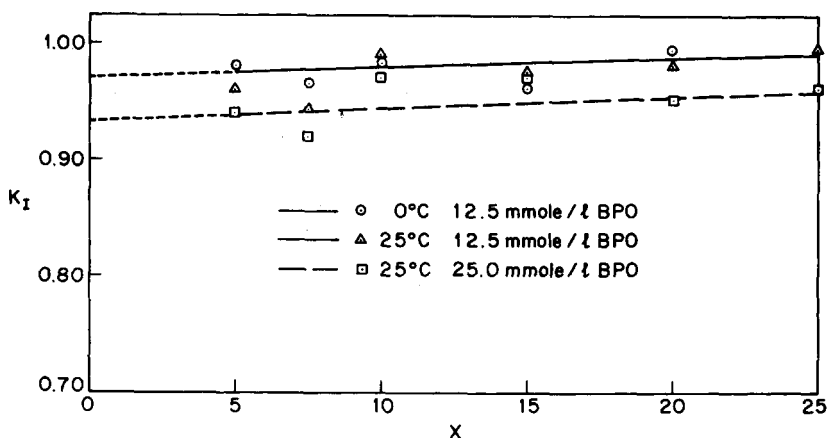Fig. 2. Distribution of AZBN between the phases.

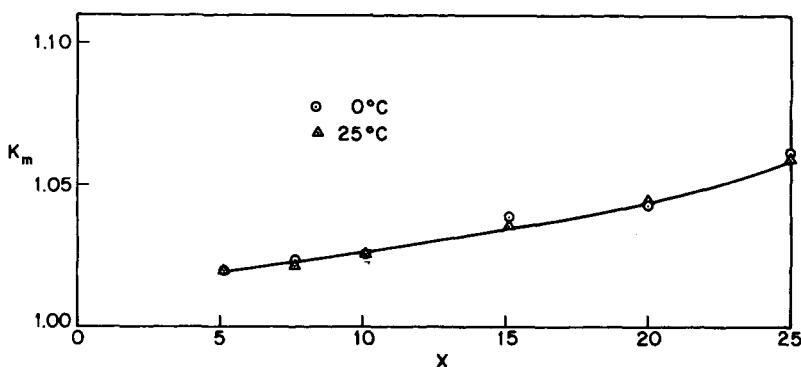Fig. 3. Distribution of BPO between the phases.

Fig. 4. Distribution of monomer between the phases.

does appear to decrease by approximately 3% as the overall initiator concentration is doubled from 12.5 to 25.0 millimoles/l. For AZBN, K_I decreases 6–7% over the conversion range 5–25% at [I] = 12.5 millimoles/l. Higher concentrations of AZBN would not dissolve completely. No significant variation in K_I with temperature was observed for either initiator, so that these results can be applied to systems reacting at 60°C—the temperature at which most kinetic studies have been performed—with a fair degree of confidence. In fact, the close correspondence between the 0° and 25°C data is a good indication of the precision of the experimental technique. The important point to note is that for these particular systems, over the range of temperature, initiator levels, and conversions studied, K_I never differed from unity by more than 15%.

The monomer distribution coefficient K_M was always slightly greater than unity, i.e., the monomer favors the rubber phase, and increased slightly with conversion (Fig. 4). No significant variation with temperature was observed.

Figure 5 plots eq. (7) for several values of K_I and K_M. The conversions corresponding to the experimentally determined values of v'' are superimposed on the abscissa. For this system, with an initial rubber concentration of 5%, maximum rate reductions would be expected in the range of conversions investigated. Nevertheless, the maximum rate reduction to be expected solely on the basis of
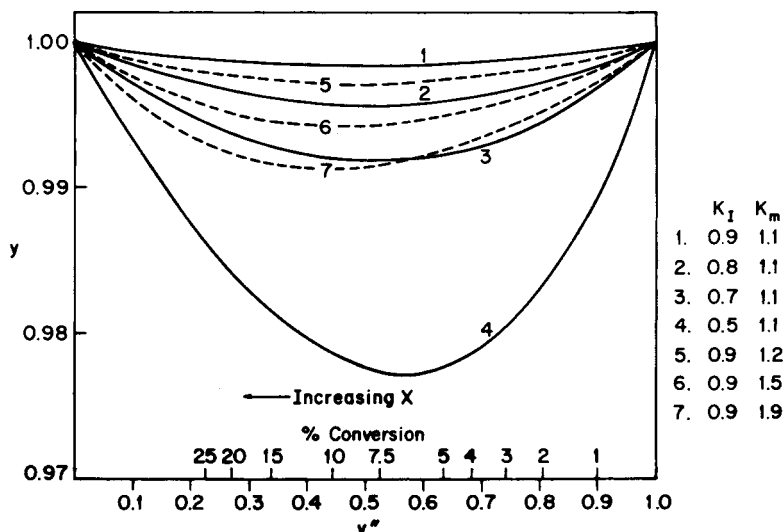
Fig. 5. Fractional rate reductions predicted by eq. (7) for distribution coefficients in the experimentally determined range.

unequal partitioning of initiator and monomer amounts to less than 1% for the experimentally determined values of K_I and K_M. Far greater rate reductions have been observed experimentally for this and similar systems. For example, Kumar[13] obtained an initial $y = 0.90$ (10% rate reduction) for 4% highly purified 35-NFA polybutadiene in styrene with BPO initiator at 60°C. Hence, another explanation for the observed rate reductions must be sought. Work is proceeding toward this end.

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