

Blocking and Copolymer Heterogeneity in Anionic Copolymerization in Industrial Reactors

RAJESH U. MEHTA* and JAMES L. WHITE, *Department of Chemical and Metallurgical Engineering, The University of Tennessee, Knoxville, Tennessee 37916*

Synopsis

An analysis is given of the effect of reactor design on the variation of composition and extent of blocking in anionic copolymerization. Batch, pipeline, continuous stirred tank (CSTR), and recycle reactors are contrasted. Specifically, alkyl lithium-polymerized butadiene-styrene and alkyl sodium-polymerized *p*-methylstyrene-styrene are contrasted to the products of copolymerization of the same monomers by free-radical mechanism. It is shown for both systems that considerably more extensive blocking occurs in a batch reactor when the anionic polymerization mechanism is used. The free-radical copolymers, unlike the anionic copolymers, exhibit compositional heterogeneity in a batch reactor. Carrying out the polymerization reaction in a pipeline reactor gives results equivalent to the batch reactor if there is plug flow. However, if a parabolic profile exists in the reactor, there will be significantly increased compositional drift in the copolymer product and a broadened molecular weight distribution, with little effect on blocking. Recycle reactors, including the recirculating loop variety, seem effective in decreasing blocking. The extent of blocking may be considerably decreased in a well-mixed continuous stirred tank reactor. However, poor mixing will greatly increase both the extent of blocking and the compositional heterogeneity of the product.

INTRODUCTION

Free-radical-polymerized butadiene-styrene copolymer (SBR), originally developed by Tschunkur and Bock¹ of I. G. Farben about 1930, has long since become the major general purpose synthetic rubber² and is the major rubber constituent of automobile tires. For a quarter century there was little change in the SBR commercially produced, except for slight variations in microstructure caused by lowering the polymerization temperature and increased control over molecular weight distribution and branching gained by the same temperature lowering and by experience.² During the late 1950's and early 1960's, researchers at a number of companies, notably Phillips Petroleum, Shell Chemical, and Firestone, developed and commercialized a new series of copolymers of these two monomers. Unlike the classical free-radical SBR, which was an essentially random copolymer, the new generation of SBR's frequently possessed block structures.^{3,4} Indeed, unique combinations of mechanical properties were obtained with some of

* Present address: Tennessee Eastman Company, Kingsport, Tennessee.

these block structures. The reasons for the unique structures of these polymers was twofold—first, they were made with the new alkyl lithium anionic catalysts which yielded living polymers to which one might first add one monomer and then a second, etc., and secondly, the reactivity ratios of the two monomers in such systems were vastly different, which would tend to form copolymers even if no care were taken with the mode of monomer addition. Now, in addition to these block copolymers, random copolymers have been produced commercially using alkyl lithium catalysts. Two methods seem to have been used: (1) increasing the polarity of the solvent, which causes large changes in the reactivity ratio, (2) improved methods of reactor design. The former method has a perhaps deleterious effect in that the butadiene microstructure is varied (1,2-addition increased) by the polar additive.⁵ Such an increase in 1,2-addition causes an increase in the glass transition temperature.⁶ It is the purpose of this paper to explore the effect of reactor design on the structure of copolymers produced by anionic mechanisms.

The effect of reaction conditions on the structure of copolymers has long been a subject of serious consideration. In the mid 1940's, Alfrey and Goldfinger⁷ and Mayo and Lewis⁸ developed an expression for the instantaneous composition of free-radical copolymer formed from a mixture of monomers in a batch reactor, and the latter integrated the equation to obtain the variation of copolymer composition with conversion. There has been considerable effort since that time to analyze the course of free-radical copolymerization with conversion, time, and position in batch,⁹⁻¹³ continuous stirred tank (CSTR),¹⁴⁻¹⁶ pipeline,^{15,17} and recycle^{18,16} reactors. This work applies to free-radical copolymerization but not to anionic copolymerization where there is no termination step, and presumptions of steady states of various types are often trivial or not meaningful. (There is a steady state concentration of active species during the latter stages of anionic polymerization resulting from zero initiation as well as termination steps.) It is the purpose of this paper to present an analysis of anionic copolymerization in various reactor types, with special attention being given to the problems of extent of blocking and composition distribution and drift. While there have been some theoretical studies of the kinetics of anionic polymerization published in the literature,¹⁹⁻²² the methods and conclusions are sometimes confusing and in any case incomplete. There has been notably little attempt to quantitatively come to grips with the problem of blocking in anionic copolymerization and its variation with reactor type and conversion. In this paper we will proceed by developing specific analyses for anionic polymerization processes and contrasting the response of two monomer systems: butadiene-styrene and styrene-*p*-methylstyrene.

CHARACTERIZATION OF BLOCKING

The problem of quantitative characterization of blocking in copolymers has attracted attention in recent years, and there has been some effort to

relate it to free radical polymerization kinetics.²³ The procedure we will follow here is an extension of that of Bovey,²⁴ which more or less derives from the ideas of Alfrey and Goldfinger.⁷ The mole fraction of A units occurring in sequences of n members is

$$F(A, n) = \frac{nP(n)}{\Sigma nP(n)} \quad (1)$$

where $P(n)$ is the probability that a monomer sequence chosen at random will contain n and only n units. Now,

$$P(n) = P_{aa}^{n-1}P_{ab} = P_{aa}^{n-1}(1 - P_{aa}) \quad (2)$$

where P_{aa} is the probability that a monomer A will add to a growing chain whose terminal unit is of the A type. Substitution of eq. (2) into eq. (1) and carrying out the summation ΣnP_{aa}^n yields²⁴

$$F(A, n) = nP_{aa}^{n-1}(1 - P_{aa})^2. \quad (3)$$

However, to get a measure of blocking, one does not need simply $F(A, n)$ but rather the total fraction of A in blocks having at least n but perhaps $(n + 1)$ or more units. Consider the quantity F_{nA} which is defined as the mole fraction of A units possessing $\left(\frac{n-1}{2}\right)$ A units adjacent to each side of it in the macromolecule. (Here n is taken to be odd.) This quantity is

$$\begin{aligned} F_{nA} &= \frac{1}{n} F(A, n) + \frac{2}{n+1} F(A, n+1) \quad (4a) \\ &+ \dots + \frac{j}{n+j-1} F(A, n+j-1) + \dots \\ &= (1 - P_{aa})^2 \sum_{j=n}^{\infty} (j - n + 1) P_{aa}^{j-1} \\ &= (1 - P_{aa})^2 P_{aa}^{n-1} \sum_{i=1}^{\infty} iP_{aa}^i \\ &= P_{aa}^{n-1}. \quad (4b) \end{aligned}$$

F_{nA} with a large enough n value should be a reasonable representation of blocking. We shall arbitrarily take $n = 5$ here.

KINETICS OF ANIONIC COPOLYMERIZATION

Consider an anionic initiator such as an organometallic compound, denoted by I, to initiate the simultaneous interpolymerization of monomers A and B. The rate of consumption of these monomers in a batch reactor would be

$$-\frac{d[A]}{dt} = k_{ia}[A][I] + k_{aa}(A)[IA^*] + k_{ba}[A][IB^*] \quad (5a)$$

$$-\frac{d[B]}{dt} = k_{ib}[B][I] + k_{bb}[B][IB^*] + k_{ab}[B][IA^*] \quad (5b)$$

where $[X]$ is the concentration of any species X and IA^* represents an active species with a terminal unit derived from the A monomer.

For alkyl lithium polymerization in hydrocarbon solvents, the growing chain seems to largely exist in a dimeric form which dissociates to form the active species that reacts with the monomer,^{3,4} and

$$[IA^*] = K_A[(IA^*)_2]^{1/2} \text{ and } [IB^*] = K_B[(IB^*)_2]^{1/2} \quad (6)$$

where $[IA^*]$ and $[IB^*]$ are but small fractions of the $[(IA^*)_2]$ and $[(IB^*)_2]$ concentrations. Similarly, the alkyl lithium initiator largely exists in an inactive associated form, perhaps a hexamer. Only the dissociated I can initiate polymerization, and thus $[I]$ in eq. (5) should be replaced with $[(I)_6]^{1/6}$.

As time proceeds during an anionic polymerization, the initiator concentration $[I]$ goes to zero and the active species concentration $[IA^*] + [IB^*]$ becomes equal to $[I](0)$. The instantaneous monomer and polymer incorporation compositions are determined by the four propagation rate constants k_{aa} , k_{ba} , k_{bb} , and k_{ab} . The copolymerization propagation rate constants are generally expressed in terms of reactivity ratios^{7,8}:

$$r_1 = \frac{k_{aa}}{k_{ab}} \quad r_2 = \frac{k_{bb}}{k_{ba}} \quad (7)$$

It is to be noted that unlike free-radical polymerization there is no termination, and if there is monomer incorporation composition drift with time, this does not imply a heterogeneous product but rather a composition drift along the polymer chains.

Perhaps, the first critical look at how one might simplify the kinetics of ionic copolymerization was given a generation ago by Landler,¹⁹ who suggested a certain relationship between propagation rate constants. Landler argues that the competition between the two monomers toward the attacking ion should be independent of the nature of the monomer last added to the chain (terminal unit) and proposed that therefore

$$k_{ab} = k_{bb} \quad \text{and} \quad k_{ba} = k_{aa} \quad (8a)$$

or

$$r_1 = \frac{1}{r_2} \quad (8b)$$

Relationships between propagation rate constants in anionic copolymerization were later considered by O'Driscoll²⁰ and O'Driscoll and Kuntz,²¹ who disputed Landler's contention and eq. (8a), on the basis of experiments by Graham, Dunkelberger, and Goode²⁵ on monomers with different polarity. O'Driscoll in his first paper considers the importance of discriminating terminal units and in particular the case where the cross-over rate constants k_{ab} and k_{ba} are near zero. O'Driscoll and Kuntz note that for monomers of

similar polarity, eq. (8b) is a reasonably good approximation while eq. (8a) is not necessary. They replace this with the expressions

$$k_{aa} = xk_{ba} \quad k_{bb} = \frac{1}{x} \cdot k_{ab} \quad (8c)$$

which are also compatible with eq. (8b).

In the remainder of this paper we will accept eqs. (8b) and (8c). We now turn to the details of reactor design.

REACTOR ANALYSIS

Batch Reactor

The batch reactor and other reactor systems considered are summarized in Figure 1. Consider an anionic copolymerization taking place in a homogeneous test tube or beaker in which there are initial concentrations of initiator of $[I](0)$ and of the two monomers $[A](0)$ and $[B](0)$. As time proceeds, the initiator starts chains of IA^* and IB^* , and these propagate gradually depleting the monomer until at 100% conversion only a concentration of $[I](0)$ active chains remain. The solution of the problem of anionic copolymerization necessitates knowledge of the following: (1) the

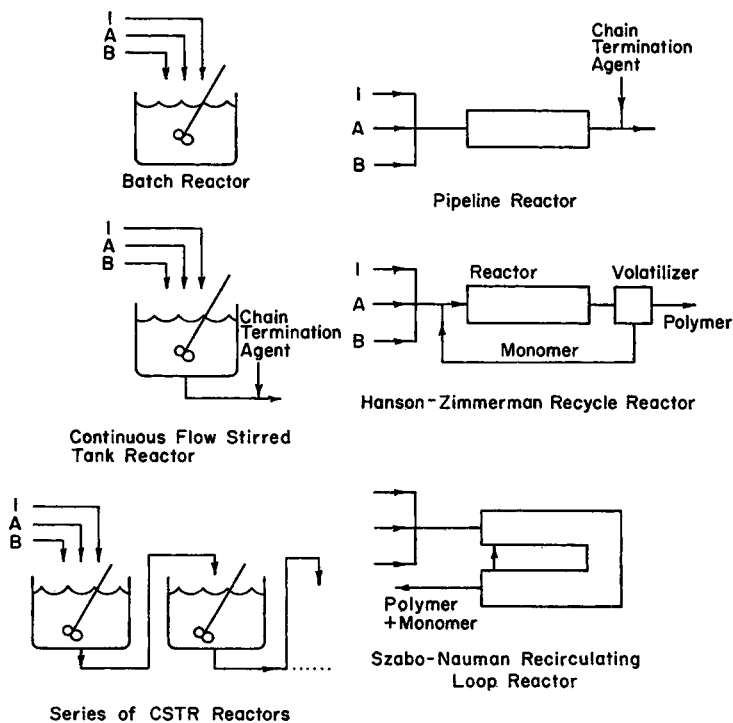


Fig. 1. Copolymerization reactors.

depletion of monomer as a function of time, (2) the composition and extent of blocking in the copolymer as a function of conversion.

If we define the instantaneous mole fraction of A being incorporated to the copolymer as F_1 and f_1 as the instantaneous mole fraction of A in the unreacted monomer, then from the ratio of eq. (5a) to (5b), neglecting the initiation steps, and applying eq. (8b), we obtain

$$\frac{F_1}{1 - F_1} = \frac{1}{r_2} \left(\frac{f_1}{1 - f_1} \right) \quad \text{or} \quad F_1 = \frac{f_1}{1 + r_2(1 - f_1)} \quad (9)$$

where no presumptions of a steady state have been made. The average copolymer composition, \bar{F}_1 , of the fraction C of the monomer that has been converted is

$$\bar{F}_1 = \frac{f_1(0) - (1 - C)f_1}{C} \quad (10)$$

with

$$C = 1 - \frac{[A] + [B]}{[A](0) + [B](0)} \quad (11)$$

It may be shown using the methods of Skeist⁹ and Meyer and Lowry¹⁰ that the instantaneous copolymer composition varies with conversion according to²⁶

$$C = 1 - \left[\frac{f_1(t)}{f_1(0)} \right]^{(r_2/1 - r_2)} \left[\frac{1 - f_1(t)}{1 - f_1(0)} \right]^{(1/1 - r_2)} \quad (12)$$

The variation of conversion with time may be computed. For the special case²⁶ of $x = 1$, we obtain

$$\ln \frac{[A](0)}{[A](t)} = \ln \left[\frac{f_1(0)}{f_1(t)} (1 - C) \right] = k_{aa}[I](0)t + \frac{(k_{ia} - k_{aa})[I](0)}{k_{ia}[A](0) + k_{ib}[B](0)} \left[1 - e^{-[k_{ia}[A](0) + k_{ib}[B](0)]t} \right] \quad (13a)$$

while for arbitrary x ,

$$\ln \left[\frac{f_1(0)}{f_1(t)} \left(\frac{1 - f_1(0)}{1 - f_1(t)} \right)^{r_1} (1 - C)^{1 - r_1} \right] = \frac{(k_{ia} - r_1 k_{ib})[I](0)}{k_{ia}[A](0) + k_{ib}[B](0)} \left[1 - e^{-[k_{ia}[A](0) + k_{ib}[B](0)]t} \right] \quad (13b)$$

Equations (13) are obtained by the same methods as those applied to free-radical copolymerization by O'Driscoll and Knorr.¹² However, no presumption of steady states has been made. It turns out that, at least for some of the systems considered in our calculations, eq. (13b) yields something of the order zero equal to zero, for all conversions and times. This is due to its being developed by subtraction of two similar equations, such as

lead to eq. (13a), in an intermediate step in the derivation. This subtraction may be avoided by use of a steady hypothesis, i.e., $k_{ab}[IA^*][B]$ is equal to $k_{ab}[IB^*][A]$. If this be assumed, it may be shown that²⁶:

$$\begin{aligned} \frac{-d\ln[A]}{dt} &= \frac{k_{aa}}{x} \left[1 + (x-1) \left/ \left(1 + \frac{x}{r_1} \frac{[B]}{[A]} \right) \right. \right] [I](0) \\ &+ \left[k_{ia} - \frac{k_{aa}}{x} \left[1 + (x-1) \left/ \left(1 + \frac{x}{r_1} \frac{[B]}{[A]} \right) \right. \right] \right] [I](0) e^{-[k_{ia}[A](0) + k_{ib}[B](0)]t}. \end{aligned} \quad (14)$$

In the special case when $\frac{x}{r_1} \frac{[B]}{[A]}$ is small, eq. (14) may be integrated to give an expression in every way equivalent to eq. (13a), except that k_{aa} is replaced by k_{aa}/x .

Finally, the blocking factor F_{nA} developed in eq. (9) at any time t in the course of the reaction is

$$F_{nA} = \left[\frac{k_{aa}[A]}{k_{aa}[A] + k_{ab}[B]} \right]^{n-1} = \left[\frac{r_1 f_1}{r_1 f_1 + (1 - f_1)} \right]^{n-1}. \quad (15)$$

Pipeline Reactor

To a first approximation, the formalism developed for the batch reactor may be directly applied to the pipeline reactor. Instead of considering the time variation of a segment of stationary reacting fluid, one follows the residence time of a fluid element as it traverses through the reactor. If the velocity profile is flat, one may directly use the equations in the previous section.^{17,27} However, if the system is isothermal and in laminar flow, the velocity profile will be approximately parabolic. This will result in both composition heterogeneity and a broadened molecular weight distribution. Generally, the non-Newtonian characteristics of the reacting fluid (it is a polymer solution) will tend to give it a flatter velocity profile.^{28,29} However the long residence-time polymers near the wall of the pipe will have a higher molecular weight than the material with the shorter residence times near the centerline. Thus, the outer layers will have a higher zero shear viscosity^{30,31} than the fluid at smaller radii, and the molecular weight effect will counteract the non-Newtonian viscosity and make the velocity profile more parabolic than might be expected. (A similar effect operates in free-radical polymerization where the higher conversions, though of similar molecular weight if the Norrish-Smith gel effect³² is unimportant, are at the larger radii. Here the increase of viscosity with concentration produces the effect.) If there is significant heat of polymerization and viscous dissipation, the temperature build-up will tend to lower the viscosity in this region and counteract this effect. Diffusion of the monomer radially outward from the lower conversion core will have a similar viscosity-reducing influence. It is interesting in this regard to study the recent investigation of anionic polymerization in a tubular reactor by Lynn and Huff.³³

The equations of the previous section remain valid, but the residence time now varies with radius. In particular, the average composition of the copolymer, \bar{F}_1 , is the flow rate average,

$$C_p \bar{F}_1 Q = \int_0^R 2\pi r V \bar{F}_1 C_b(t) dr \quad (16)$$

where C_p is the conversion for a tubular reactor and $C_b(t)$ is the conversion for a batch reactor after residual time t . If a parabolic velocity profile is presumed, it may be shown that \bar{F}_1 may be expressed³⁴ as follows:

$$C_p \bar{F}_1 = 2 \left(\frac{x}{V_0} \right)^2 \int_{t/V_0}^{\infty} \frac{\bar{F}_1(t)}{t^3} C_b(t) dt \quad (17)$$

where V_0 is the centerline velocity.

Continuous Flow Stirred Tank Reactor (CSTR)

One of the most important of industrial reactors for polymerization processes is the stirred tank into which a steady flow of initiator and monomer occur and out of which a continuous stream of polymer and unreacted monomer move.^{27,35} Models of varying sophistication of the processes occurring in this reactor have been developed through the years. The simplest model is that of *perfect mixing*, i.e., the concentrations in the reactor are spatially homogeneous and one may proceed by considering the reacting mixture to just spend a period of time V/Q , where V is the reactor volume in this constant environment. Denbigh³⁵ worked out the problem of homopolymerization in this reactor model, and various authors^{14,15,16} have considered free-radical copolymerization. There are two basic problems that must be resolved: (1) the relationship of monomer conversion to residence time, and (2) the variation of copolymer composition with conversion. The conversion of monomer A is related to residence time through

$$[A]_0 - [A] = \left[k_{ia} + k_{ia}k_{aa}\theta[A] + k_{ia}k_{aa}\theta[B] \right] [A][I]\theta \quad (18)$$

where $[A]_0$ is the concentration of A entering the reactor, θ is V/Q , and $[X]$ is the concentration of X within and exiting the reactor. The composition of the copolymer formed in the reactor is

$$F_1 = \bar{F}_1 = \frac{f_1}{f_1 + r_2(1 - f_1)} \quad (19a)$$

and conversion C is related to depletion of A by

$$C = 1 - \frac{(1 - f_1^0)}{(1 - r_2)(1 - f_1)} + \frac{r_2 f_1^0}{(1 - r_2)f_1} \quad (19b)$$

A second model is that of *complete segregation*,²⁷ wherein the reacting fluid is considered to consist of isolated globules that behave as individual

reactors and spend various amounts of time within the reactor depending upon some residence time distribution. Tadmor and Biesenberger³⁶ have applied this model to homopolymerization and O'Driscoll and Knorr,¹⁶ to free-radical copolymerization. It has frequently been speculated that this type of model should work better than that for perfect mixing in high-viscosity polymerization systems. Nagata et al.³⁷ have carried out an experimental study of this problem with the polymerization of styrene. These authors conclude that the type of impeller used in the mixing seems to have an enormous effect. (As shown by the experiments of Giesekus,³⁸ the viscoelastic characteristics of polymer solutions induce major variations in the mixing patterns caused by impellers in tanks. It is not known how this affects residence time distributions.) If mixing is poor and significant segregation occurs, the copolymer emerging from the reactor will be heterogeneous and possess not only a mixture of compositions but a broadened molecular weight distribution. This is similar to the effect of a velocity distribution in a tubular reactor, but the situation may become more extreme. In a perfectly segregated reactor, the average polymer composition is

$$C_e \bar{F}_1 = \int_0^{\infty} g(t) \bar{F}_1 C_b(t) dt \quad (20)$$

where C_e and $C_b(t)$ have similar meaning to the terms in eq. (16) and $g(t)$ is the residence time distribution, which is approximately $e^{-t/\theta}/\theta$.

Recycle Reactor

Hanson and Zimmerman¹⁸ describe the Dow development of a pipeline reactor containing a monomer recycle stream which enables one to produce free-radical copolymers with enhanced compositional uniformity. The exiting reaction mixture is run through a volatilizer and the volatilized monomer is recycled. This pushes the composition of the monomers entering the reactor toward that of the exiting polymer. If we let $[A]_0$ be the concentration of monomer A entering the system and $[A]_r$, the concentration of A in the recycle stream, then the actual concentration of A, $[A]_i$, in the beginning of the reactor will be

$$R[A]_i = [A]_0 Q + [A]_r (R - Q) \quad (21)$$

where Q is the volumetric flow rate of the fluid entering the reactor and R is the volumetric flow rate within the reactor. The conversion of such a reactor will be 100%. Szabo and Nauman¹⁵ discuss a variant on this, called a *recirculating loop* reactor, in which no volatilizer is used and the polymer is recycled along with the monomer. This gives rise to $[A]_r$, the recycle concentration being equal to the exit concentration and the total conversion being

$$C = 1 - \frac{[A]_r + [B]_r}{[A]_0 + [B]_0} \quad (22)$$

One may consider the equations of normal pipeline reactors to hold throughout both of these recycle reactors. For anionic copolymers, at least, there will be a significant difference between the character of the polymers produced in the two reactor systems. In the recirculating loop reactor, polymer is recycled and some of the reactive species will have very long residence times. This will lead to an increase in both the molecular weight of these species and the width of the molecular weight distribution not found in a normal pipeline or Hanson-Zimmerman recycle reactor. The magnitude of blocking will be decreased, but multiple block (4, 6, etc., blocks) will be formed in living copolymers which are recirculated.

Equation (21) may be rewritten as

$$f_{A1} = \frac{f_A^0 + f_A \phi (R/Q - 1)}{1 + \phi (R/Q - 1)} \quad (23)$$

where ϕ is the fraction of monomer in the recycle. For the recirculating loop reactor, this is from eq. (22) simply $(1 - C)$. For the plug flow model, C may be calculated from eq. (12).

CALCULATIONS

Butadiene-Styrene*

The composition and extent of blocking of anionic (alkyl lithium) and free-radical polymerization of butadiene and styrene in various reactor

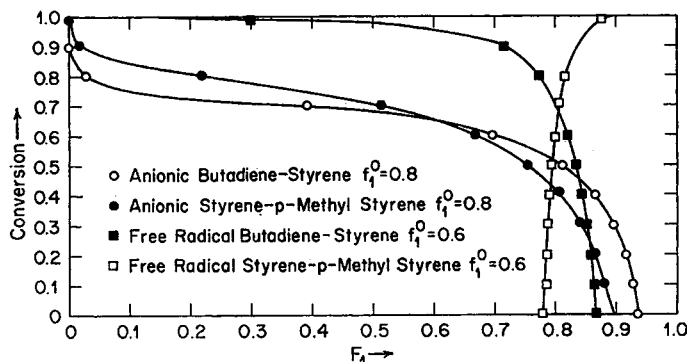


Fig. 2. Conversion-instantaneous composition curves for copolymerization in a batch reactor.

designs have been worked out. The rate constants and reactivity ratios for anionic and free-radical copolymerization are summarized in Table I. The initial monomer concentrations have been computed so as to yield approximately 75 wt-% (82 mole-%) butadiene copolymer at 70% (mole average)

* We have not considered in anionic copolymerization the association of growing chains and initiator molecules. Furthermore the results for free-radical copolymerization do not correspond to industrial practice for this system, because the reaction is generally carried out in emulsion rather than in the solution or bulk states.²

TABLE I
Rate Constants and Reactivity Ratios in Anionic and Free-Radical Copolymerization

Monomer system	Ref.	Solvent	Temp, °C	Catalyst	k_{aa} , l./mole sec	k_{bb} , l./mole sec	$r_1 = k_{aa}/k_{ab}$	$r_2 = k_{bb}/k_{ba}$	k_{ia} , l./mole sec	k_{ib} , l./mole sec
Butadiene-styrene	39	toluene	25-30	anionic (Li ⁺)	0.05	0.13	10.0	0.1	0.0088	0.0141
Styrene- <i>p</i> -methylstyrene	40	THF	25	anionic (Na ⁺)	950	210	5.3	0.18	very large	very large
Butadiene-styrene	41	insensitive	50	free radical	65	103	1.48	0.23	—	—
Styrene- <i>p</i> -methylstyrene	42	insensitive	50	free radical	195	189	0.83	0.96	—	—

conversion in a batch reactor. This was found to necessitate an 80 mole-% charge in the case of free-radical polymerization and a 60 mole-% for the anionic copolymer. Figures 2-6 plot the instantaneous mole fraction of butadiene in the copolymer and the mole fraction F_{5A} of butadiene units having at least a segment of two butadiene units adjacent to each side of it versus conversion. From these figures we see that in the free-radical copolymer, the variation of the mole fraction of butadiene is only from 0.87

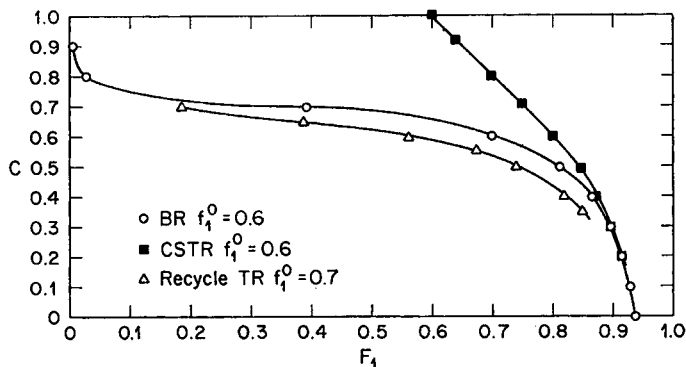


Fig. 3. $C-F_1$ curves for anionic copolymerization of butadiene-styrene in different types of reactors.

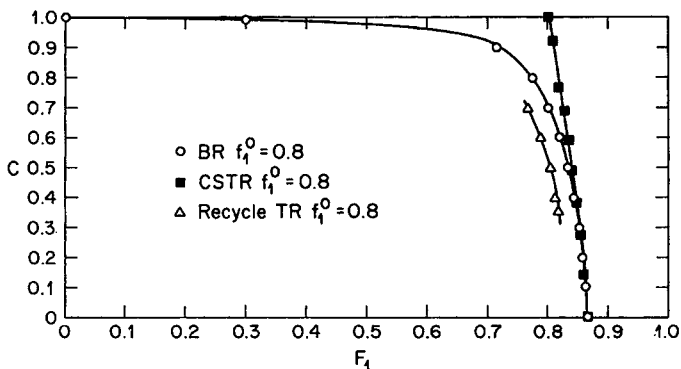


Fig. 4. $C-F_1$ curves for free-radical copolymerization of butadiene-styrene in different types of reactors.

to 0.80, and the blocking factor F_{5A} varies from 0.53 to 0.35. For the alkyl lithium polymer, on the other hand, the instantaneous butadiene content varies from 93.6% at zero conversion to 87% at 40% conversion to 39% at 70% conversion (and to 5% at 80% conversion if the reaction were continued). The butadiene blocking factor drops from 0.81 at zero conversion to 0.04 at 70% conversion. (At 80% conversion there would be a blocking factor of 0.90 for the styrene.) It should be remarked again that the composition and blocking drifts for the free-radical polymers represent a

variation in structure of different molecules produced at increasing stages of the polymerization. The drifts for the anionic case represent a variation in composition along the length of each molecule. Both the free-radical and anionic copolymers produced in a batch reactor are compositionally uniform

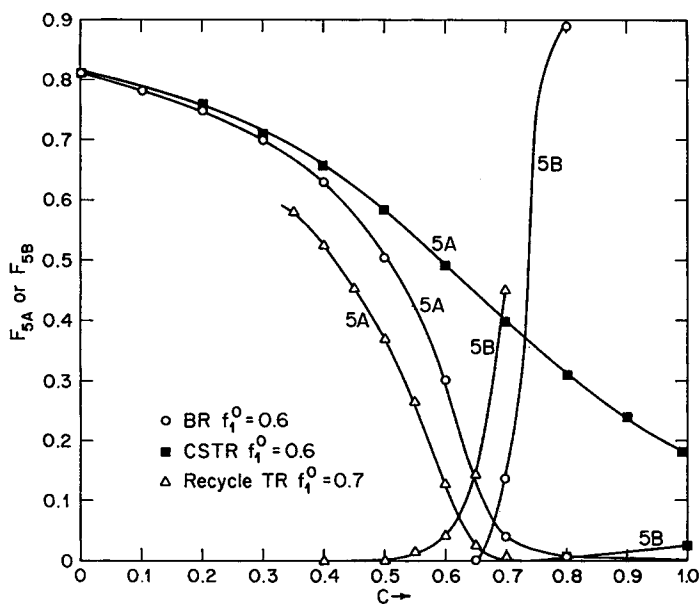


Fig. 5. F_{5A} and F_{5B} vs. C curves for the anionic copolymerization of butadiene-styrene in different types of reactors,

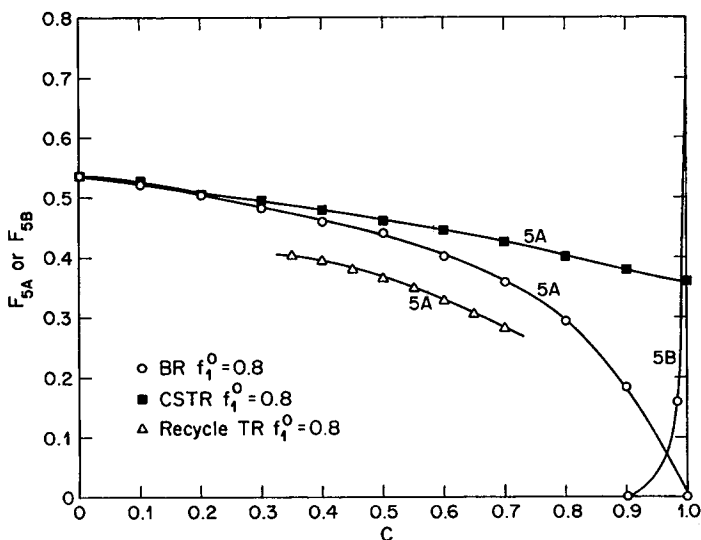


Fig. 6. F_{5A} and F_{5B} vs. C curves for free-radical copolymerization of butadiene-styrene in different types of reactors.

from molecule to molecule. However, the anionic copolymer has in essence a butadiene block and a high-styrene end.

The composition of copolymer emerging from one pipeline reactor will be to a first approximation the same as for a batch reactor. However, the velocity profile will introduce greater compositional and molecular weight heterogeneity. For a parabolic velocity distribution, we have divided the anionic copolymer into three weight fractions depending upon radial position. Analytically we have done this rewriting the integrals of eqs. (16) and (10) as summations and considered the \bar{P}_1 at different sections of the radius. The 25 wt % lowest conversion globules exiting from the central core will have an average of 92.5% butadiene in the product; the medium conversion globules will contain 91.1% butadiene; and finally, the 50 wt % highest conversion globules near the wall will consist of 65.5% butadiene. The final product will be a mixture of these three fractions. The high-butadiene, low-conversion fraction coming out of the central core will be low molecular weight material, having remained in the reactor approximately one half the average residence time. The copolymer from the outer annuli will have high molecular weight, but lower butadiene content.

Turning now to a single CSTR reactor, we find that for a homogeneous, perfectly mixed reactor, addition of the same monomer distribution as in a batch reactor (80 mole-% butadiene in the free-radical case) results in an 85.2% butadiene free-radical copolymer and a 75.2% butadiene anionic copolymer. In the case of the free-radical copolymer 0.425 of the butadiene is in pentad blocks, and in the anionic case, 0.40 is. We thus seem to achieve a random anionic copolymer. However, this would seem to be illusory and dependent upon perfect mixing assumption. In particular, if the reactor behaves as a completely segregated CSTR, it will behave as thousands of batch reactors in parallel with a residence time distribution of $e^{-t/\theta}/\theta$. If we divide the exiting product anionic copolymer into four equal weight fractions, low, medium low, medium high, and high conversion globules, we find that these fractions will have an average butadiene content of 88.6%, 79%, 77%, and 65.5%, respectively. The low-conversion globules will contain a high percentage of butadiene. The high-conversion globules will consist of molecules containing high styrene content blocks at one end.

Finally, we have examined the structure of copolymers made in a recycle reactor, specifically of the Szabo-Nauman recirculating loop variety. The net effect of the recycle is to cut down on the concentration gradient along the length of the reactor. This should strikingly decrease the extent of blocking, and indeed it does. Figures 5 and 6 show the variation of composition and blocking along the length of such a reactor for a recycle ratio of 2.0. It is seen that the composition gradient in the copolymer is decreased. The initial fraction of pentad blocks of butadiene in the anionic copolymer drops from 0.81 for the same monomer ratio in a batch or plug flow reactor to 0.58. This is about the initial value for free-radical copolymers in the batch or plug flow reactor.

Styrene-*p*-Methylstyrene

The composition and extent of blocking of anionic (sodium alkyl) and free-radical polymerization of styrene and *p*-methylstyrene were also determined for a series of reactors. Monomer-inlet compositions were determined so as to make an 80 mole-% styrene copolymer at 70% conversion. The results are generally similar to, though less striking than, those for the butadiene-styrene system. Figures 2 and 7 through 10 show the variation of the instantaneous copolymer compositions and extent of blocking with conversion in a batch reactor. For the free-radical copolymer, the composition varies from 77.7% to 80.5% styrene, while for the anionic copolymer the variation is from 89.3% to 50.8%. The styrene blocking factor varies from 0.35 to 0.40 for the free-radical copolymer and from 0.62 to 0.07 in the anionic copolymer. Again we have relatively uniform, more or less random free-radical copolymer and an anionic copolymer which tends to have a block form.

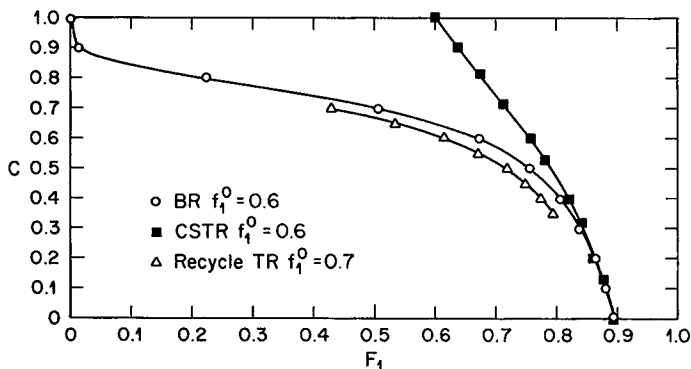


Fig. 7. C - F_1 curves for anionic copolymerization of styrene-*p*-methylstyrene in different types of reactors.

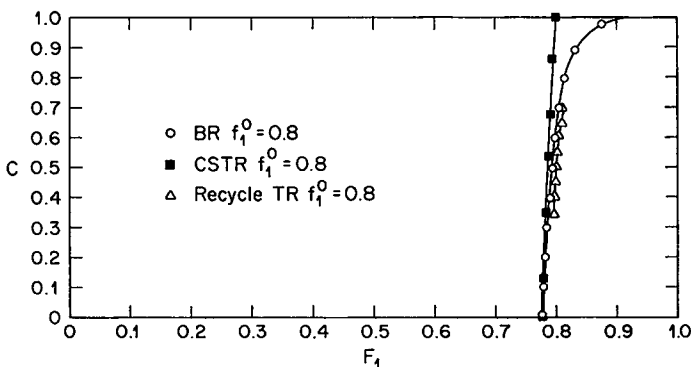


Fig. 8. C - F_1 curves for free-radical copolymerization of styrene-*p*-methylstyrene in different types of reactors.

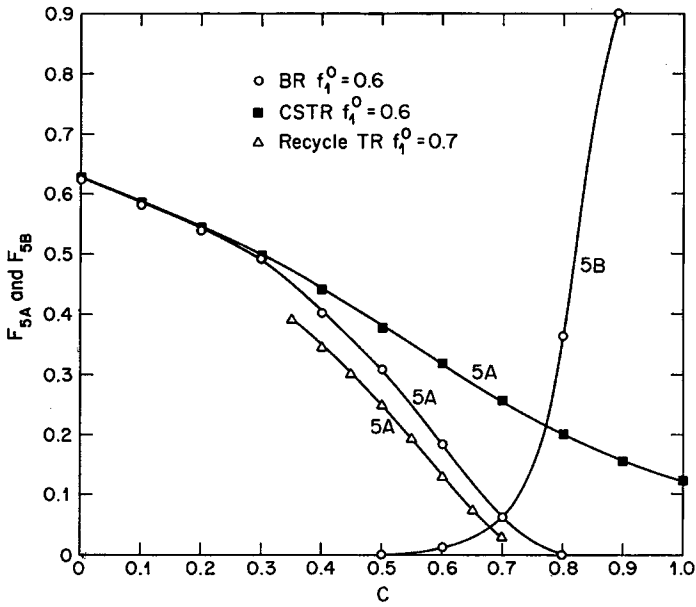


Fig. 9. F_{5A} and F_{5B} vs. C curves for anionic copolymerization of styrene-*p*-methylstyrene in different types of reactors.

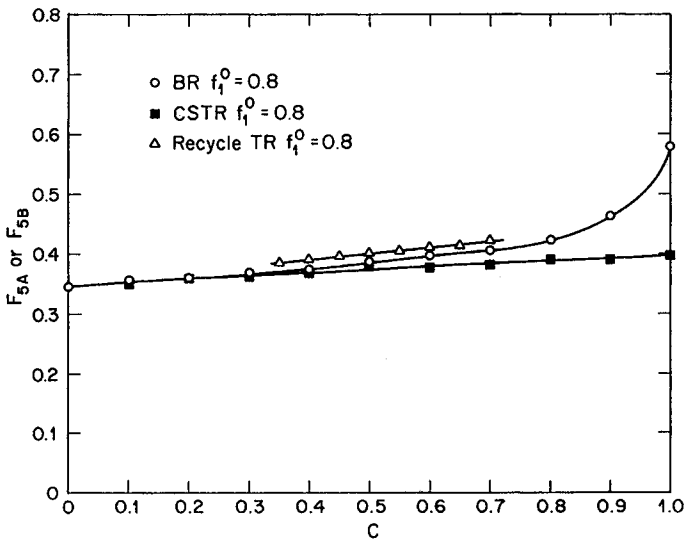


Fig. 10. F_{5A} vs. C curves for the free-radical copolymerization of styrene-*p*-methylstyrene in different types of reactors.

The pipeline reactor again yields the same results as the batch reactor when the plug flow asymptote is used. Once again, assuming Bosworth's laminar flow residence time distribution, if the exiting anionic copolymer is divided into three weight fractions, the low-conversion 25 weight-% globules from the central core will contain 87.1% styrene, the medium-conversion 25% globules will contain 74.8% styrene, and the high-conversion 50% globules near the wall will contain a lower, 61.7% styrene.

If the same monomer composition that entered the batch reactor is added to a single homogeneous, perfectly mixed CSTR, at 70% conversion the free-radical copolymer will be 79.4% styrene and the anionic copolymer will be 72.1% styrene; 38.2% of the styrene in the free-radical copolymer and 25.6% of the styrene in the anionic copolymer will exist in pentad blocks. A random anionic copolymer with no composition gradient along its length is obtained. Again, we must make the point that this result depends upon the perfect mixing assumption. If the CSTR is segregated, once again the approximate effect of segregation may be indicated by dividing the exiting copolymer into four equal weight fractions, low-, medium-low-, medium-high-, and high-conversion globules. These globules will contain 85.6%, 78.8%, 72.2%, and 65.6% styrene, respectively. While the low-conversion fraction will have low molecular weight and high styrene content, the high-conversion globules will tend to have high molecular weight and contain blocks of *p*-methyl styrene.

As seen in Figures 7-10, a similar, increased uniformity of composition is produced in this copolymer with a recycle reactor. For the recirculating loop variety with a recycle ratio of 2.0, the initial fraction of styrene pentad blocks is decreased from 0.62 to 0.39.

CONCLUSIONS

Analyses of the kinetics and extent of block formation in anionic copolymerization based upon the O'Driscoll-Kuntz hypothesis have been developed for batch, pipeline, CSTR, and recycle reactors. The extent of block formation is greater in anionic as opposed to free-radical copolymerization in batch reactors. It was shown that compositional homogeneity will tend to deteriorate in pipeline reactors more than in batch reactors. On the other hand, considerable improvement in compositional uniformity and indeed significant decreasing of the extent of block copolymer may be obtained by introducing a recycle into a pipeline reactor. CSTRs will show greatly differing performance depending upon the extent of mixing. Perfect mixing of a homogeneous material will lead to rather uniform anionic copolymers. Segregation effects will lead to significant blocking and compositional heterogeneity. Variables such as impeller design and speed of stirring probably will be important here.

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