Effect of Synthesis Conditions on the Rheological Properties of Styrene Butyl Acrylate Copolymers

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Synopsis

The chemical and physical properties of synthetic polymers depend strongly on the polymerization process. This fact is even more determinant when dealing with copolymers. Styrene/butyl acrylate copolymers were synthesized using an emulsion copolymerization process. The amount of initiator, emulsifier, and transfer agent were varied in a systematic way in order to establish the relationship between polymerization conditions and rheological properties of the molten copolymers. Rheological and molecular weight results show that the different polymerization conditions have important effects on the properties of the final copolymer mainly through the development of different sequence distributions of the monomeric units in the copolymer chain. These results have been interpreted in terms of the kinetic mechanisms that explain the emulsion copolymerization processes. Furthermore, the rheological characterization is used as an additional tool in establishing the different structure of the resulting copolymers.

INTRODUCTION

The importance of the flow behavior of materials has one of its more evident manifestations during processing. This behavior is determined by specific molecular characteristics, which in practice are dependent primarily on the chemical nature of the polymers and on polymerization conditions.[1]

Copolymerization processes are very relevant to the industrial environment because they allow the preparation of polymers of different compositions that can be used in a wide variety of applications. It is well known that the copolymer properties are determined by their molecular weight distributions and the nature, relative quantities, and arrangement of the monomeric units along the chains.[2] However, all the above-mentioned facts depend on the type of copolymerization process used.

Emulsion copolymerization is a quite complex process due to the many components that form the reaction medium, i.e., initiator, emulsifier, electrolyte, transfer agent, etc.[3]

The initiator plays a key role in the case of heterogeneous polymerizations. The corresponding free radicals are produced in the aqueous phase and react with the fraction of monomers soluble in this phase. The oligoradicals formed become hydrophobic and can react to form new particles or be absorbed by previously formed micelles or particles. In any case the principal reaction site is the dispersed colloidal phase monomer–polymer.

The ability of the system to increase the number of colloidal monomer–polymer particles is proportional to the amount of emulsifier present. The global rate of reaction (i.e., the sum of the rate of reaction of the individual particles) increases for both the micellar and homogeneous mechanisms. In the latter case the emulsifier only serves as a stabilizer of the primary particles formed in the aqueous phase.

The molecular weight characteristics of emulsion copolymerization products are basically a function of: monomer composition, reaction temperature, radical/particle ratio (proportional to initiator and emulsifier), final conversion, and chain transfer agent concentration.

The number of radicals/particle/time increases with initiator concentration. This fact would result in a decrease in the molecular weight of the product. On the other hand, an increase in emulsifier content results in a decrease in the number of radicals/particle/time; therefore, the molecular weight would show an increase. These considerations are only valid in the absence of chain transfer agent. When this component is present, all possible combinations of the above-mentioned phenomena have to be taken into account.

In the case of copolymers it is important to further point out that the properties of the final product will not only depend on the molecular weight distribution and the global composition, but also on the development of the microstructure (distribution of monomeric sequences in the copolymer chain) as a function of time. Due to this fact synthetic copolymers are a mixture of different copolymers with global composition depending on the degree of conversion.

The St/BuA system is particularly interesting due to the nature of its components. Styrene is a highly hydrophobic monomer that follows the theory of Smith–Ewart (case II). Butyl acrylate is a more polar and water-soluble monomer that has the tendency to polmerize initially in the water phase, forming particles in a direct way instead of going through the micellar mechanism.

Only a few reports in the literature[4-7] have dealt with the system's kinetics and its relation to the properties of the final copolymers.

The purpose of this paper is to present a study that relate some of the kinetic parameters, i.e., initiator, emulsifier, and transfer agent, with, on one hand, the molecular characteristics and, on the other, the flow behavior (in the molten state) of the resulting copolymers.

Experimental Program

Synthesis

The styrene–butyl acrylate copolymers were synthesized using a batch emulsion polymerization process. A 2-L glass reactor equipped with a stirrer (250 rpm) and a set of baffles to promote good mixing of the reaction medium was used throughout this study.

The monomers were distilled under nitrogen prior to their use. The initiator, potassium persulfate (PPS), emulsifier, lauryl sodium sulfate (LSS), electrolyte, sodium carbonate (SoCa), and transfer agent, n-dodecyl mercaptan (n DM), were used as received from the supplier.

In all cases the reaction was carried out under a nitrogen atmosphere and the reaction time was held constant (180 min). The kinetics of the reaction was monitored using gas chromatography (analysis of the unreacted monomers as a function of time).[8] The global conversion was a function of the emulsifier, initiator, and transfer agent levels.

The final copolymers were coagulated by adding the latex, drop by drop and with agitation, to an equivalent volume of ethyl alcohol. After filtration the copolymers were dried in a vacuum oven at 60°C for 24 h.

The final products, after coagulation, can still contain inorganic residues inherent to the emulsion polymerization process as well as a small fraction of residual monomers. In order to eliminate these impurities, the following purification procedure was used. The copolymer was dissolved in acetone and the inorganic residues were eliminated by decantation. As a second step the copolymer was precipitated using an equivalent volume of methanol followed by filtration of the mixture. The organic impurities remained in the acetone–methanol mixture. Subsequently, the copolymer was dried in a vacuum oven (at the same conditions mentioned above). No thermal stabilizer was added.

Two different copolymer compositions, 90/10 and 50/50 (w %) styrene/butyl acrylate, were used in order to elucidate the effect of different concentrations of initiator, emulsifier and transfer agent. A summary of the experimental conditions is given in Table I.

Characterization of the Copolymer

Molecular Weight

The molecular weight of the purified final copolymers was measured using gel permeation chromatography, GPC (Waters, Model R401). For columns of μ-styragel with pore sizes of 10^6, 10^5, 10^4, and 10^3 Å were eluted with THF.

A universal polystyrene calibration was used, and therefore the molecular weight results reported in this paper are not absolute values.

TABLE I
Experimental Conditions[a]

Run	Monomers (g)		PPS (mg)	LSS (g)	n-DM (g)	SC (g)	H_2O (g)	T (°C)
	St	BuA						
I1	50	50	75	4	0.5	4.0	600.0	60
I2	50	50	105	4	0.5	4.0	600.0	60
I3	50	50	120	4	0.5	4.0	600.0	60
E1	90	10	90	2	0.5	4.0	600.0	60
E2	90	10	90	4	0.5	4.0	600.0	60
E3	90	10	90	6	0.5	4.0	600.0	60
E4	90	10	90	8	0.5	4.0	600.0	60
TA1	90	10	105	4	0	4.0	600.0	60
TA2	90	10	105	4	0.7	4.0	600.0	60
TA3	90	10	105	4	1.05	4.0	600.0	60

[a] PPS = potassium persulfate; LSS = lauryl sodium sulfate; n-DM: n-dodecyl mercaptan; SC = sodium carbonate.

It should also be mentioned that our molecular weight results were not corrected for composition variations. However, for a given composition (90/10 or 50/50 wt%) it is possible to establish a comparison among the samples and determine, although in a relative way, the influence of the kinetic parameters on the molecular weights and its distribution.

Rheological Properties

A Rheometrics Viscoelastic Tester was used to obtain the viscoelastic material properties, i.e., complex viscosity (η^*), storage modulus (G'), and loss tangent (tan δ) as a function of frequency. The test mode was small amplitude oscillatory shear[9] with parallel plate fixtures ($D = 5$ cm) and frequency varying from 0.1 to 100 rad/s. The strain was set at 10%. This value of strain was chosen in order to record a large stress response but within the linear viscoelastic range. This assumption was verified by running samples at lower strain values (1,3,5, and 7%).

Since the samples were not thermally stabilized, several samples were retested in order to detect degradation; the results did not point out a change in properties.

Results and Discussion

Effect of Initiator

A detailed study of the kinetics of this system[8] showed that the copolymerization rate increased as the initiator content increased in a pattern similar to the one predicted by the Smith–Ewart theory.[10] Furthermore, the final global conversion increased (I1 = 88%, I2 = 91%, I3 = 99%). Since these global conversions are similar, one would expect similar molecular weight distributions and cumulative compositions. this fact is confirmed by the molecular weight characterization given in Table II.

Figures 1 and 2 show the complex viscosity (η^*) and storage modulus (G') results. The complex viscosity increases as the amount of initiator increases. The changes are considerable both in magnitude and overall flow behavior. At low initiator contents the copolymer exhibits Newtonian behavior over a wide frequency range. As the initiator increases the range of Newtonian behavior narrows until the flow behavior can be described in terms of the power law.

The storage modulus increases with the amount of initiator and its frequency dependence diminishes. Furthermore, the tan δ results show that

TABLE II
Molecular Weight Characteristics[a]

Sample	Initiator (PPS) (mg)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	($\overline{M}_w/\overline{M}_n$)
11	75	12,200	38,700	87,800	3.1
12	105	13,900	42,600	96,000	3.2
13	120	13,400	40,100	84,100	2.9

[a] St/BuA = 50/50.
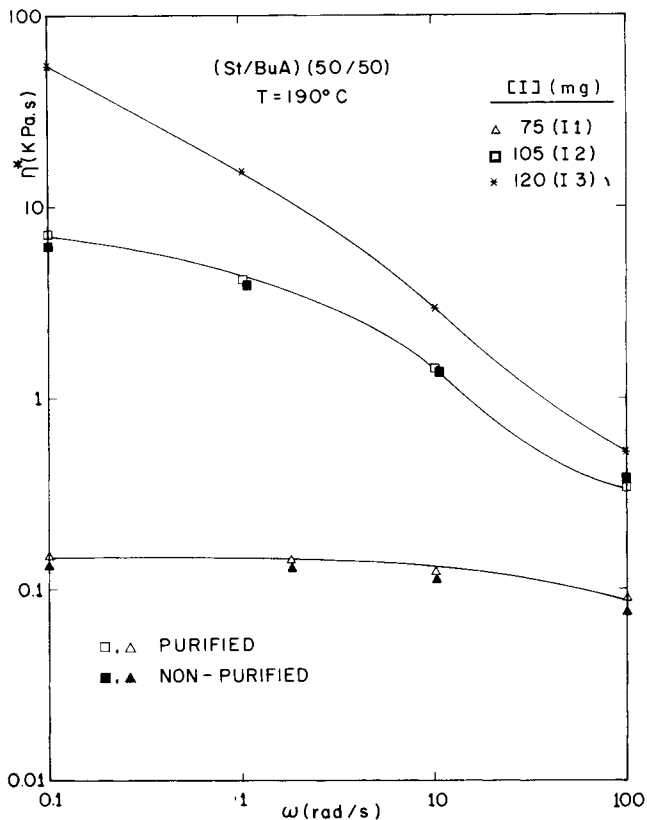
Fig. 1. Complex viscosity vs. frequency. Effect of initiator. [I] (mg): ($\triangle$) 75 (I1); ($\square$) 105 (I2); (*) 120 (I3); ($\square$, $\triangle$) purified; ($\blacksquare$, $\blacktriangle$) nonpurified.

in the case of low initiator content the flow behavior (over the whole frequency range) is governed by the viscous component, tan $\delta > 1$. On the other hand, samples I2 and I3 show crossover frequencies that decrease with increasing initiator content, with sample I3 almost completely dominated by the elastic component.

It should be pointed out that the dynamic measurements were capable of detecting differences in flow behavior for materials having close values of MWD and different $\overline{M}_w$'s (Table II).

Since the experimental frequency window is fixed, the results given in Figures 1 and 2 correspond to different regions of the viscoelastic response as given by dinamic measurement.

Sample I1 displays a behavior approaching the terminal region of behavior ($G' \propto \omega^2$, $G'' \propto \omega$); this corresponds roughly to frequencies lower than that of the crossover point. Samples I2 and 3 exhibit behaviors that can be more closely related to the high frequency end of the terminal zone and into the plateau region (dynamic moduli approximately independent of frequency). Unfortunately, due to experimental limitations it was not possible to measure the dynamic moduli at lower frequencies, which whould have allowed a direct comparison of all samples in the terminal zone. This
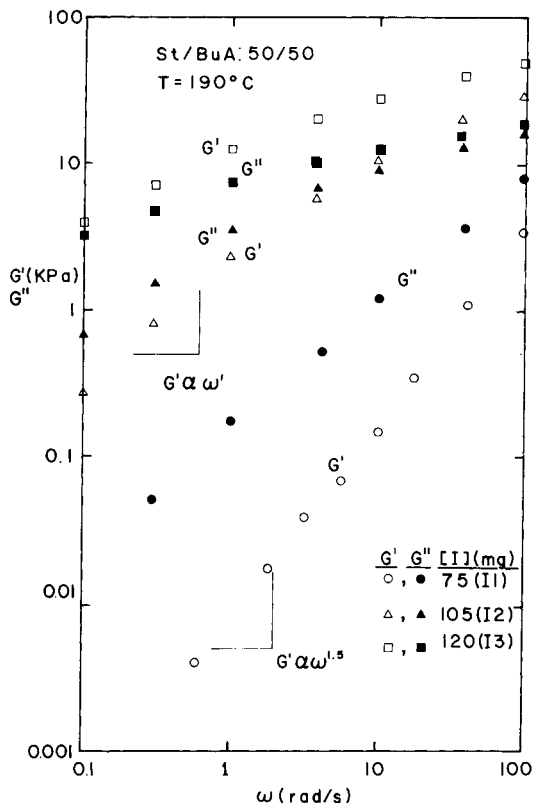
Fig. 2. Storage and loss modulus vs. frequency. Effect of initiator. [I] (mg): (○, ●) 75 (T1); (△, ▲) 105 (I2); (□, ■) 120 (I3); (○, △, □) G'; (●, ▲, ■) G''.

fact is particularly important since the low frequency response can be related to the $\overline{M}_w$ and molecular weight distribution.

However, the relative molecular characterization combined with the dynamic measurements can provide qualitative indications of the way the amount of initiator can change the flow behavior, i.e., the molecular structure of the samples.

Figure 3 shows a Cole–Cole plot for samples I1–13. Previous research[11–15] has shown that this plot is independent of $\overline{M}_w$ and that it can be used to detect differences in flow behavior of samples with similar molecular weight charaacteristics.

Among the factors considered as the cause of the differences we can cite the degree and size of branching and crosslinking effects. In the case of copolymers we could still add two other factors, i.e., sequence distribution and chemical heterogeneity.

Both styrene and butyl acrylate have small polymer transfer constants at the reaction temperature (60°C), and therefore the probability of developing branches in the copolymers in the final stages of the reaction is very low. On the other hand, the increase in the initiator content and the high conversions obtained could favor the growing of side chains. Samples show-
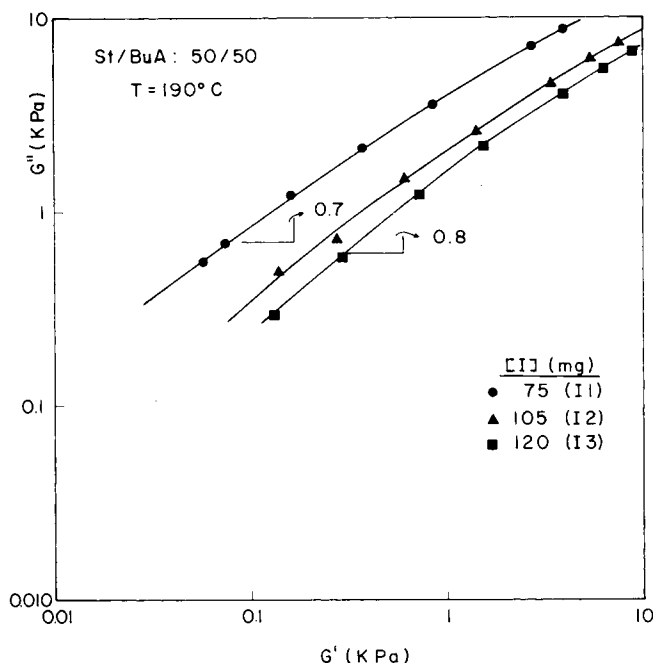
Fig. 3. Cole–Cole plot. Effect of initiator. [I] (mg): (●) 75 (I1); (▲) 105 (I2); (■) 120 (I3).

ing extensive branching would show insoluble fractions when dissolved in THF; this situation was not encountered in our GPC tests. It should be mentioned that this test is not conclusive since during the purification process the high molecular weight fractions could have been eliminated. An alternative rheological characterization was made using raw and purified samples (Fig. 1). The results show the same behavior of both samples, and therefore we conclude that even in the presence of branching the chemical microstructure should be the dominant factor in the flow behavior.

It was mentioned earlier that the molecular weight results were in agreement with the final values of the final global conversion. However, even if these parameters are similar, the instantaneous composition and the dyad distributions can be quite different.

The system styrene/butyl acrylate has very different reactivity ratios, $r_{St} = 0.69$ and $r_{BuA} = 0.18$; this implies a chemical heterogeneity as a function of conversion. The only exception to this rule is the azeotropic composition (33 mol % styrene) in which the copolymers formed have the same sequence distribution along the entire process.

In the case of styrene compositions (in the feed) larger than the azeotropic composition the initial copolymer will be richer in styrene than in butyl acrylate. This trend is reversed at higher conversions where the butyl acrylate has a larger polymerization rate.

To characterize the polymer microstructure, we have to use experimental methods such as ^{13}C-NMR or theoretical predictions based on probability theory applied to the polymerization process.

It can be shown[1] that the cumulative values of the distribution of dyads as a function of conversion can be obtained as follows:

$$P(M_i M_j)_{\text{cum}} = \frac{\int_0^\gamma P(M_i M_j)\, d\gamma}{\int_0^\gamma d\gamma} \tag{1}$$

where $i, j = 1,2$.

$P(M_i M_j)$ represents the terminal conditional probability of monomers M_i and M_j forming dyads $M_i M_j$. γ is the global conversion given by $\gamma = [(M_1)_0 + (M_2)_0 - (M_2)]/[(M_1)_0 + (M_2)_0]$. the integration of eq. (1) for the 50/50 (wt %) copolymers is shown in Table III.

The initial copolymer has a composition close to 62 mol % styrene. As the reaction proceeds between 88% (I1: 58.3% St-accumulated) and 91% global conversion, an additional 3% of copolymer containing 50% St is polymerized; when a 93% (I3:57.6% St-accumulated) global conversion is reached, 2% of a copolymer with only 40% St is still being added. In general, the theoretical predictions given in Table III show that above a global conversion of 85% the instantaneous dyad distribution shows a large change particularly in the case of St–St and BuA–BuA dyads. The same trend can be detected in the triad formation. The final copolymers should be considered as a "mixture" of all the products formed at the different stages of the reaction; this chemical and structural heterogeneity should be the cause of differences in flow behavior.

Butyl acrylate has an elastomeric character, and therefore the presence of an increased number of its dyads will manifest itself in a copolymer with enhanced elastic properties. This hypothesis is confirmed by the $G'-G''$ results where copolymer I3 ($\tan \delta < 1$) shows a more elastic behavior than copolymer I1 ($\tan \delta > 1$).

Finally, it should be mentioned that the failure in trying to correlate GPC results and viscoelastic properties most probably has to do with the inaccuracies involved in the chromatographic determinations of complex systems such as the copolymers presented in this work. On the other hand it emphasizes the possibility of using the rheological characterization as a tool to discriminate between polymers prepared under different reaction conditions.[17]

Effect of the Emulsifier

The molecular weight characteristics of the resulting copolymers are given in Table IV. In a similar pattern to the one encountered in the analysis of the initiator, the amount of emulsifier does not influence the development of molecular weight in a significant way. It has to be pointed out that the copolymers prepared with variable amounts of emulsifier show high values of $\overline{M}_w$ and MWD. This is only a consequence of the copolymer monomer ration (90/10 St/BuA).

Figure 4 shows the η^* results. There is no clear trend concerning the dependence of complex viscosity and emulsifier content, particularly in the

TABLE III
Composition and Dyad Distribution[a]

Global conversion (MOL %)	Composition (mol %)				Distribution of dyads (%)						Distribution of triads (%)			
	Instantaneous		Cumulative		Instantaneous			Accumulated			Instantaneous		Accumulated	
	St	BuA	St	BuA	AA	AB	BB	AA	AB	BB	AAA	BBB	AAA	BBB
0.0	61.7	38.3	61.7	38.3	0.283	0.668	0.049	0.283	0.668	0.049	0.130	0.006	0.130	0.006
5.0	61.6	38.4	61.6	38.4	0.280	0.670	0.049	0.282	0.669	0.049	0.128	0.006	0.129	0.006
10.0	61.3	38.7	61.5	38.5	0.277	0.672	0.050	0.280	0.670	0.050	0.125	0.007	0.127	0.006
20.0	60.9	39.1	61.3	38.7	0.271	0.677	0.053	0.277	0.672	0.051	0.120	0.007	0.125	0.007
30.0	60.4	39.6	51.1	38.9	0.262	0.684	0.055	0.273	0.675	0.052	0.114	0.008	0.122	0.007
40.0	59.7	40.3	60.8	39.2	0.250	0.689	0.059	0.269	0.678	0.053	0.105	0.009	0.119	0.007
50.0	58.9	41.1	60.5	39.5	0.239	0.698	0.063	0.264	0.681	0.055	0.097	0.010	0.115	0.008
60.0	57.7	42.3	60.1	39.9	0.223	0.707	0.070	0.258	0.684	0.057	0.086	0.011	0.111	0.008
70.0	56.1	43.9	59.7	40.3	0.200	0.719	0.080	0.252	0.688	0.059	0.072	0.015	0.106	0.009
80.0	53.5	46.5	59.1	40.9	0.166	0.732	0.100	0.243	0.694	0.063	0.052	0.026	0.101	0.010
85.0	51.2	48.8	58.7	41.3	0.140	0.739	0.121	0.238	0.696	0.066	0.038	0.030	0.098	0.011
86.0	50.6	49.4	58.6	41.4	0.134	0.740	0.127	0.236	0.696	0.067	0.035	0.032	0.097	0.011
88.0	49.2	50.8	58.3	41.7	0.119	0.738	0.142	0.224	0.698	0.068	0.029	0.040	0.096	0.011
90.0	47.4	52.6	58.1	41.9	0.100	0.734	0.165	0.231	0.698	0.070	0.022	0.051	0.094	0.012
92.0	44.8	55.2	57.8	42.2	0.080	0.719	0.200	0.228	0.710	0.073	0.014	0.072	0.092	0.014
94.0	40.7	59.3	57.5	42.5	0.053	0.678	0.268	0.224	0.700	0.077	0.007	0.118	0.090	0.016
96.0	32.7	67.3	57.0	43.0	0.021	0.546	0.432	0.220	0.696	0.083	0.001	0.265	0.088	0.020

[a] St = A; BuA = B; AB = 50/50.

TABLE IV
Molecular Weight Characteristics[a]

Sample	Emulsifier (LSS) (g)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$(\overline{M}_w/\overline{M}_n)$
E1	2	12,000	103,000	587,000	8.5
E2	4	12,000	105,000	662,000	8.8
E3	6	11,500	107,000	598,000	8.2
E4	8	12,000	94,000	768,000	7.9

range of LSS between 2 and 6 g. The flow behavior can be described as power law in the complete range of frequencies. Copolymers E1, E2, and E3 show very close values of η^* at the low frequency end of the measurements. These results agree, in a qualitative way, with the molecular weight parameters given in Table IV.

Figure 5 shows the storage modulus, G' results for the minimum and maximum level of emulsifier. the behavior of both samples is similar with crossover frequencies (ω_c) increasing with emulsifier content.

Figure 6 shows the corresponding Cole–Cole plot. In this case samples E2, E3, and E4 appear to form a single master curve. This implies that the molecular structure of these copolymers has to be considered very similar ($\overline{M}_v$, MWD, sequence distributions).

At the start of the reaction the copolymer formed has a 89.5 mol % styrene content. As the conversions reaches 90% the composition is around 91 mol
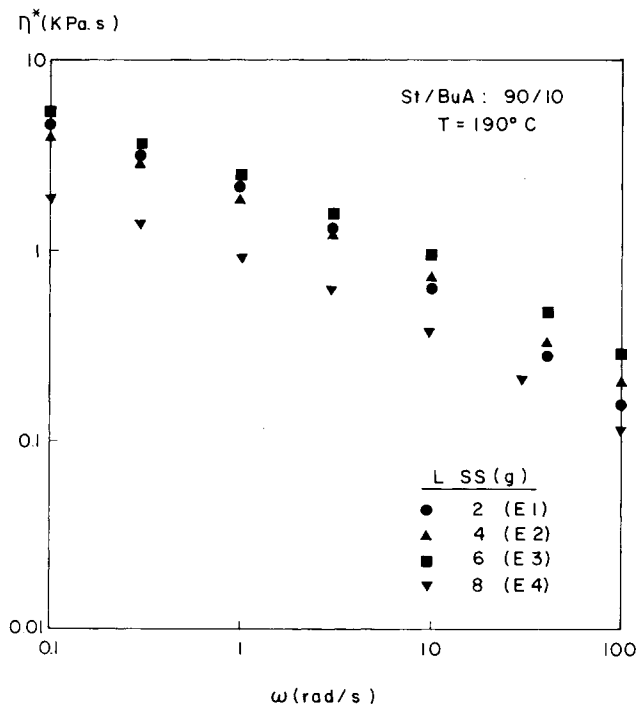

Fig. 4. Complex viscosity vs. frequency. Effect of emulsifier. LSS (g): (●) 2 (E1); (▲) 4 (E2); (■) 6 (E3); (▼) 8 (E4).
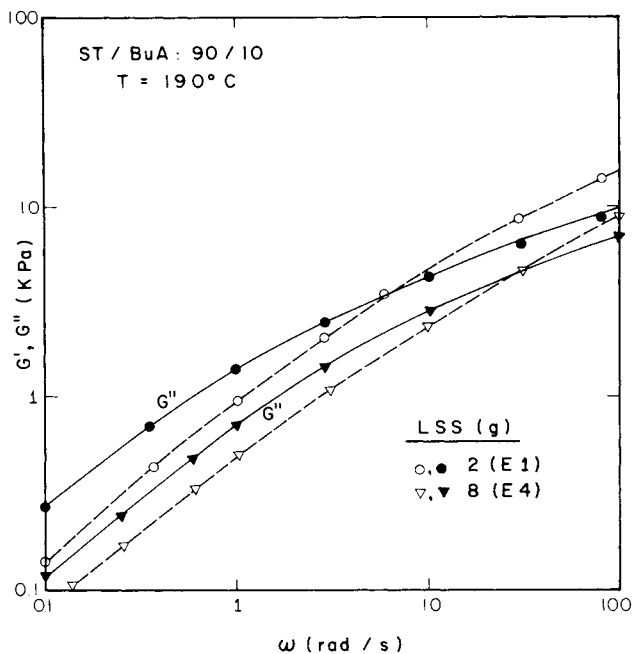
Fig. 5. Storage and loss modulus vs. frequency. Effect of emulsifier. LSS (g) (○,●) 2 (E1); (▽, ▼) 8 (E4).
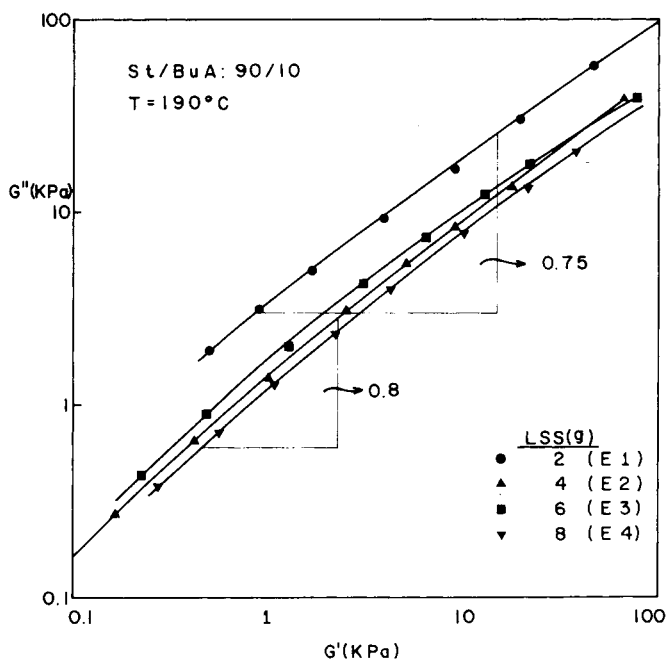
Fig. 6. Cole–Cole plot. Effect of emulsifier. LSS (g): (●) 2 (E1); (▲) 4 (E2); (■) 6 (E3); (▼) 8 (E4).
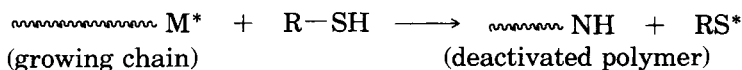
% styrene. The composition and theoretical prediction of the microstructure are given in Table V. From them we can conclude that the dyad distribution and chemical heterogeneity vary within a very narrow range and therefore are less important in determining the viscoelastic properties of the final product.

Effect of the Transfer Agent

In this section we report the results obtained while varying the amount of transfer agent. In order to observe the behavior of a limiting case sample TA1 was copolymerized in the absence of transfer agent. The molecular characteristics of these samples are given in Table VI. It has to be mentioned that the sample prepared without n-DM could not be dissolved, and therefore no molecular weight data are available. This fact is an indication of a material with very high molecular weight. The results for the other two copolymeres show that both $\overline{M}_w$ and MWD decrease as the amount of transfer agent increases. These materials having the same copolymer composition as the ones analyzed for the effect of the emulsifier are characterized by a much broader molecular weight distribution.

Figure 7 show the results of the complex viscosity (η^*) as a function of frequency. The data are in agreement with the molecular weight results. As the amount of transfer agent increases the viscosity shows a drastic decrease and the flow behavior becomes less non-Newtonian. Most probably this is due to the role played by the transfer agent as a controlling factor in limiting the size of the chain.

We can assume that the average time between two radicals entering a colloidal particle, is sufficiently large, allowing many chain transfer reactions to the n-DM within the particle:

$$\text{⌇⌇⌇⌇⌇⌇ M}^* \quad + \quad \text{R—SH} \quad \longrightarrow \quad \text{⌇⌇⌇ NH} \quad + \quad \text{RS}^*$$
(growing chain)   (deactivated polymer)

It will appear that the radical RS* starts again the propagation of copolymer chains without affecting the rate of reaction. Therefore, the molecular weight distribution is controlled exclusively by the concentration of n-DM within the colloidal particles and not by the radical/particle ratio.

Figure 8 shows the storage and loss modulus as a function of frequency. In the case of sample TA1 the viscoelastic behavior is dominated by the elastic component. For samples TA2 and TA3 we find crossover frequencies that increase with the amount of n-DM present. In these cases the overall viscoelastic behavior is similar but the magnitude of the elastic component decreases as the n-DM increases.

A Cole–Cole plot is given in Figure 9. Within experimental error the data for the three copolymers form a single master curve. This behavior is in agreement with the fact that data presented in a Cole–Cole plot form a single master curve independent of $\overline{M}_w$ only if they have similar MWD and structural characteristics.

Therefore, it appears that the transfer agent affects both the level of molecular weight as well as the polydispersity of the copolymers without significantly changing the molecular architecture.

TABLE V
Composition and Dyad Distribution[a]

Global conversion (mol %)	Composition (mol %)				Distribution of dyads (%)						Distribution of triads (%)			
	Instantaneous		Cumulative		Instantaneous			Accumulated			Instantaneous		Accumulated	
	St	BuA	St	BuA	AA	AB	BB	AA	AB	BB	AAA	BBB	AAA	BBB
0.0	89.5	10.5	89.5	10.5	0.792	0.206	0.002	0.792	0.206	0.002	0.700	0.000	0.700	0.000
5.0	89.6	10.4	89.5	10.5	0.794	0.204	0.002	0.793	0.205	0.002	0.703	0.000	0.702	0.000
10.0	89.7	10.3	89.6	10.4	0.796	0.202	0.002	0.794	0.204	0.002	0.707	0.000	0.704	0.000
20.0	90.0	10.0	89.7	10.3	0.802	0.196	0.001	0.797	0.202	0.002	0.715	0.000	0.707	0.000
30.0	90.3	9.7	89.9	10.1	0.809	0.190	0.001	0.800	0.200	0.002	0.724	0.000	0.714	0.000
40.0	90.7	9.3	90.0	10.0	0.816	0.183	0.001	0.803	0.195	0.001	0.734	0.000	0.715	0.000
50.0	91.1	8.9	90.2	9.8	0.826	0.174	0.001	0.806	0.192	0.001	0.746	0.000	0.720	0.000
60.0	91.7	8.3	90.4	9.6	0.835	0.164	0.001	0.810	0.188	0.001	0.752	0.000	0.726	0.000
70.0	92.3	7.7	90.6	9.4	0.848	0.151	0.001	0.815	0.184	0.001	0.778	0.000	0.732	0.000
80.0	93.2	6.7	90.9	9.1	0.865	0.134	0.001	0.820	0.179	0.001	0.803	0.000	0.740	0.000
85.0	93.7	6.3	91.1	8.9	0.877	0.123	0.001	0.832	0.176	0.001	0.819	0.000	0.714	0.000
90.0	94.5	5.5	91.2	8.8	0.892	0.108	0.000	0.827	0.172	0.001	0.841	0.000	0.748	0.000
95.0	95.5	4.5	91.5	8.5	0.915	0.085	0.000	0.831	0.168	0.001	0.874	0.000	0.755	0.000

[a] St = A; BuA = B. A/B = 90/10.

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TABLE VI
Molecular Weight Characteristics[a]

Sample	Transfer agent (n-DM) (g)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$(\overline{M}_w/\overline{M}_n)$
TA1	0		Insoluble in THF		
TA2	0.7	12,000	172,000	1,149,000	14.4
TA3	1.05	9000	104,000	1,005,000	11.5

[a] St/BuA=90/10.

CONCLUSIONS

Changes in initiator and emulsifier content did not affect significantly the molecular weight and molecular weight distribution of the final co-polymers. However, the viscoelastic properties changed significantly as the amount of initiator increased. Viscosity changed from a Newtonian to a power law flow representation. The storage modulus increased, and the viscoelastic properties switched from a viscous to an elastic dominated response.

An increase in the emulsifier content caused a small decrease in the viscosity levels; however, the flow behavior appears to be similar in all cases. The viscoelastic response is also similar and does not exhibit a definite pattern.
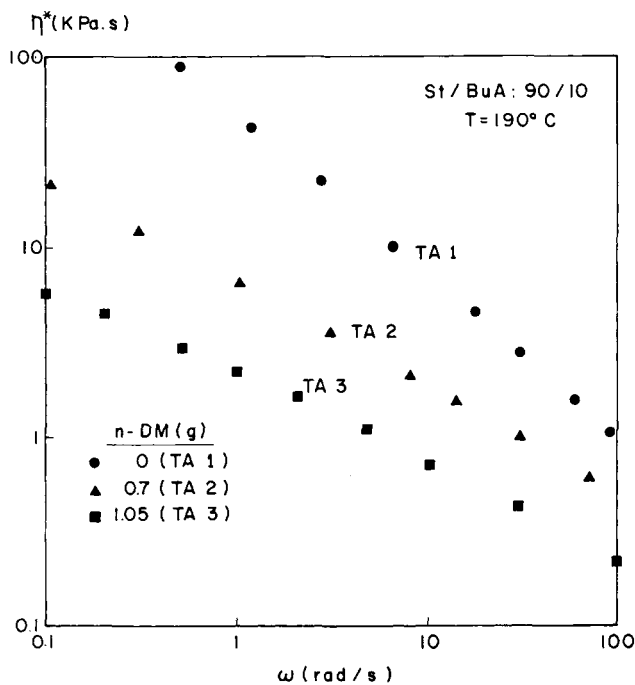

Fig. 7. Complex viscosity vs frequency. Effect of transfer agent. n-DM (g): (●) 0 (TA 1); (▲) 0.7 (TA 2); (■) 1.05 (TA 3).
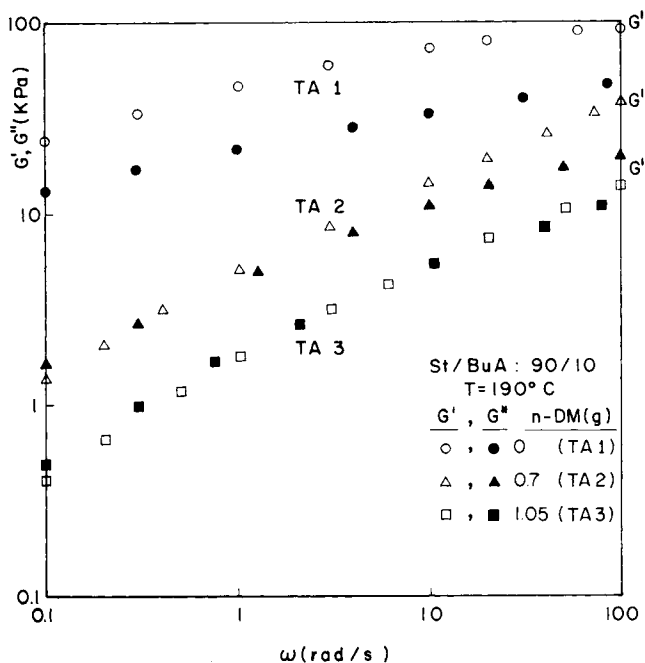
Fig. 8.   Storage and loss modulus vs. frequency. Effect of transfer agent. n-DM (g): (○, ●) 0 (TA 1); (△, ▲) 0.7 (TA 2); (□, ■) 1.05 (TA 3); (○, △, □) G'; (●, ▲, ■) G''.
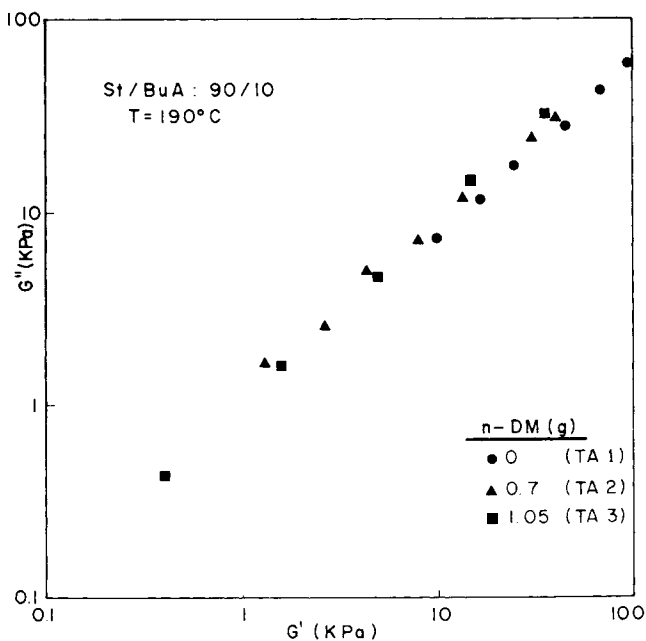

Fig. 9.   Cole–Cole plot. Effect of transfer agent. n-DM (g): (●) 0 (TA 1); (▲) 0.7 (TA 2); (■) 1.05 (TA 3).

The kinetic analysis showed that the transfer agent plays an important role in the development of the molecular weight characteristics. An increase in this parameter caused important reductions in viscosity and storage modulus.

Cole–Cole plots proved to be useful in the analysis of the effect that molecular weight characteristics and molecular architecture (sequence distribution) have on the overall viscoelastic properties of copolymers.

Finally, the results have shown that by varying some of the components of the reaction medium it is possible to obtain copolymers with similar molecular weight characteristics and different rheological properties.

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