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Radiation-Induced Graft Polymerization in Emulsion Systems

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ABSTRACT

The radiation-induced polymerization of styrene was conducted under emulsion conditions in the presence of polybutadiene latex in an attempt to induce grafting and the results were compared with the corresponding chemically initiated system. The propagation rate constants, k_p , for styrene estimated on the assumption of the Smith-Ewart theory and the activation energies derived from the temperature dependence were found to be in good agreement with the values reported in the literature. The grafting efficiency was also measured and the results are discussed in association with the molecular weight of the polystyrene chains on the basis of a simple model. This is presented to explain some aspects of the experimental results and to give clearer ideas of the reactions involved.

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Many papers have been published concerning polymerization in emulsion systems. Most of them, however, have dealt with chemically initiated polymerizations. Reports on radiation-induced polymerization in emulsion, on the other hand, have been comparatively meager. In the present paper the polymerization of emulsified styrene conducted in the presence of polybutadiene latex in an attempt to graft styrene to polybutadiene is discussed. This system is of interest from a practical point of view since it leads to high impact polystyrene which is a composite consisting of a continuous polystyrene phase and a dispersed rubber phase. The degree of real chemical bonding between the polystyrene and polybutadiene units seems to be one of the important factors for the desired improvement of the properties of the impact polystyrene. In this investigation the kinetic features and grafting efficiency are compared between radiation-induced and chemically initiated systems.

EXPERIMENTAL

Two kinds of polybutadiene latices were used: one was prepared by emulsion polymerization initiated by γ -rays at 40°C, and another was kindly supplied by the Firestone Rubber Company. The particle numbers contained in the irradiation samples were adjusted by the dilution of the original latices. The properties of the original latices are listed in Table 1. One of the important differences in the properties of these latices exists in the particle diameter. The particle diameters were measured by means of electron microscopy, the bromination technique being used to avoid the agglomeration of the particles in the process of drying the diluted latex. γ -Ray irradiation was carried out under nitrogen atmosphere with end-over-end agitation, and potassium persulfate was used as an initiator in the chemically initiated polymerizations. Extraction of homopolystyrene was conducted using cold methyl ethyl ketone as solvent. The intrinsic viscosity of the polystyrene was measured at 30°C in toluene, and molecular weights were calculated according to [1]

$$[\eta] = 12.0 \times 10^{-3} M^{0.71}$$

The solubility of styrene in polybutadiene particles was measured by the static centrifugation technique [2].

TABLE 1. Properties of Original Polybutadiene Latices

	γ -Ray prepared latex	SR-5937 latex
Particle diameter (\AA)	300	660
Polymer content (wt%)	8.5	34
Soap	Sodium lauryl sulfate	Dresinate 214 Na salt of rosin acids
Amount of soap (wt%)	2	2
Gel content	~ 0	~ 0

RESULTS AND DISCUSSION

In Fig. 1 the time-conversion curves are shown for the radiation-initiated systems with different particle numbers of the latex prepared by γ -ray irradiation. In the systems containing higher numbers of the particles the curves appear to be slightly concave to the time axis at a rather early stage of polymerization, while in the system with the lowest particle number the conversion is linear with irradiation time until higher conversions.

In Fig. 2 the conversions are plotted against reaction time for the polymerizations initiated by $K_2S_2O_8$. Both at 40 and 50°C the conversions are linear with time up to 70-80% conversion.

In Figs. 3 and 4 the kinetic curves are given for the radiation-induced systems with the Firestone SR-5937 latex. Apparently induction periods are found in the systems containing this latex. Since it was not observed in the graft polymerizations using γ -ray-prepared latex, the induction period can neither be attributed to traces of oxygen residue which were not replaced by purging with nitrogen nor to impurities involved in styrene monomer. It may probably be due to some unidentified impurities included in the latex.

Polymerizations were carried out at a lower dose rate to examine the effect of radiation intensity on the polymerization rate. The results are presented in Fig. 5. In Fig. 6 the time-conversion curves are indicated for the chemically initiated graft polymerizations to the SR-5937 latex.

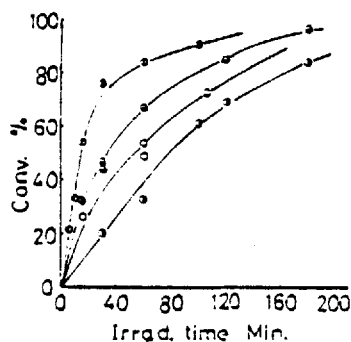


FIG. 1. The relation between the conversion of styrene polymerized in the presence of γ -ray-prepared latex and irradiation time. 0.12 Mrad/hr. Monomer to aqueous phase ratio: 1/2. (\odot) 40°C, $N = 3.2 \times 10^{15}$, ml H_2O . (\ominus) 25°C, $N = 6.7 \times 10^{15}$, ml H_2O . (\circ) 25°C, $N = 3.2 \times 10^{15}$, ml H_2O . (\bullet) 25°C, $N = 1.6 \times 10^{15}$, ml H_2O .

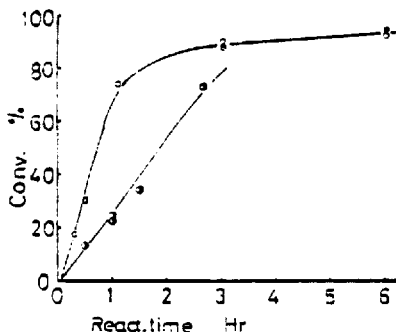


FIG. 2. Time-conversion curves for $K_2S_2O_8$ -initiated grafting of styrene to γ -ray-prepared latex. $N = 3.2 \times 10^{15}$, ml H_2O . Monomer to aqueous phase ratio: 1, 2. (\circ) 50°C, 0.5 wt% $K_2S_2O_8$. (\bullet) 50°C, 1 wt% $K_2S_2O_8$. (\ominus) 40°C, 0.5 wt% $K_2S_2O_8$.

It has been shown in some reports [3, 4] on the chemically initiated emulsion polymerization of styrene that the Smith-Ewart theory (Case II) is applicable to systems. Morton et al. [5, 6] investigated the emulsion polymerization of butadiene and found

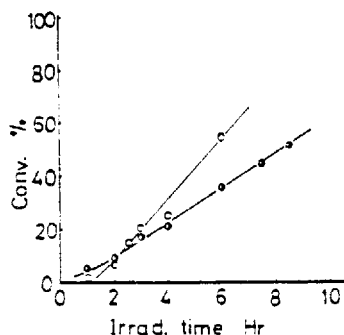


FIG. 3. Time-conversion curves for γ -ray-initiated grafting of styrene to SR-5937 latex. 0.12 Mrad/hr. 25°C. Monomer to aqueous phase ratio: 1/2. (●) $N = 3.2 \times 10^{14}$ /ml H_2O . (○) $N = 6.6 \times 10^{14}$ /ml H_2O .

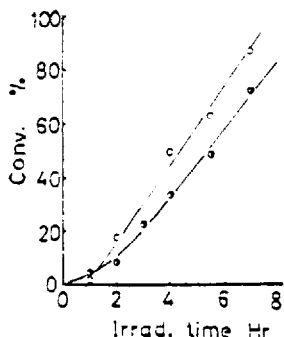


FIG. 4. Time-conversion curves for γ -ray-initiated grafting of styrene to SR-5937 latex. 0.12 Mrad/hr. 40°C. Monomer to aqueous phase ratio: 1, 2. (●) $N = 3.2 \times 10^{14}$ /ml H_2O . (○) $N = 6.6 \times 10^{14}$ /ml H_2O .

that when a hydroperoxide-polyamine redox system was employed as the initiator, the Smith-Ewart theory can be applied to the process. It would seem to be of great interest to examine the applicability of the theory to the present system.

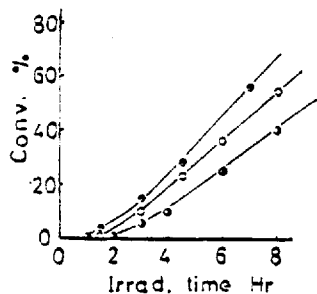


FIG. 5. Time-conversion curves for γ -ray-initiated grafting of styrene to SR-5937 latex. 0.052 Mrad/hr. Monomer to aqueous phase ratio: 1/2. (○) 25°C, $N = 3.2 \times 10^{14}/\text{ml H}_2\text{O}$. (○) 40°C, $N = 3.2 \times 10^{14}/\text{ml H}_2\text{O}$. (●) 40°C, $N = 6.6 \times 10^{14}/\text{ml H}_2\text{O}$.

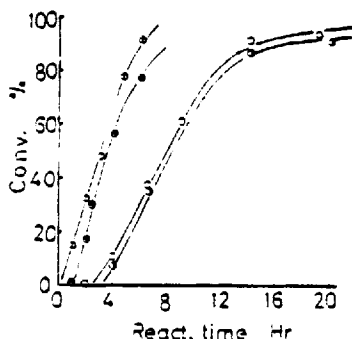


FIG. 6. The time-conversion curves for $\text{K}_2\text{S}_2\text{O}_8$ -initiated grafting of styrene to SR-5937 latex. $\text{K}_2\text{S}_2\text{O}_8$, 0.5 wt%. Monomer to aqueous phase ratio: 1/2. (○) 40°C, $N = 3.2 \times 10^{14}/\text{ml H}_2\text{O}$. (○) 40°C, $N = 6.6 \times 10^{14}/\text{ml H}_2\text{O}$. (○) 50°C, $N = 3.2 \times 10^{14}/\text{ml H}_2\text{O}$. (○) 50°C, $N = 6.6 \times 10^{14}/\text{ml H}_2\text{O}$.

According to the Smith-Ewart theory, the polymerization rate per milliliter of water is given by

$$R_p = \frac{N}{2} k_p [M] \quad (1)$$

where N refers to the number of the particles per milliliter of water, k_p to the propagation rate constant, and M to the monomer concentration in the polymer particles. To calculate the value of k_p from the kinetic data on the basis of Eq. (1), it is essential to know the value of $[M]$ in the present systems. The solubility of styrene in polybutadiene particles was estimated as follows. In the case of γ -ray-prepared latex, 1 g of polybutadiene dissolves 3.7 g of styrene, corresponding to 6.8 moles/liter of $[M]$. On the other hand, 1 g of polybutadiene in the SR-5937 latex dissolves 3.8 g of styrene, corresponding to 6.9 moles/liter. It has been reported that the solubility of monomer in polymer particles increases with particle diameter [7]. The difference in the solubility between the two latices seems to be plausible.

The values of k_p calculated from the initial slope of the kinetic curves in Figs. 1-6 are listed in Table 2. There are many values reported for k_p of styrene. The most reasonable ones obtained by Matheson et al. [8] are:

25°C	46 liter mole ⁻¹ sec ⁻¹
40°C	83
50°C	124

In Table 2 the values of k_p are almost invariable at 25°C in the γ -ray-prepared latex and the SR-5937 latex systems irrespective of the particle number or of the dose rate. Considering the relatively large error involved in the measurement of the particle diameter, the agreement may be considered as good in the systems initiated by γ -radiation at 25°C. In other systems, however, the situation is not so good as at 25°C. The experimental values are generally smaller in the chemically initiated systems, especially for the γ -ray-prepared latex. In the case of the SR-5937 latex, the values of k_p calculated for the systems containing the larger amount of the particles are approximately half of the values for the corresponding systems with the smaller amount of the particles. It should be noted that the monomer to polymer ratio in the former systems is actually a little below the saturated solubility value measured experimentally. Therefore, the calculation of k_p was achieved for these systems on the assumption that all monomer

TABLE 2. The Values of k_p (in $l \text{ mole}^{-1} \text{ sec}^{-1}$) Calculated from Kinetic Data on the Basis of Smith-Ewart Equation

	Polymerization conditions					
	Particle No.	γ -Ray initiation			$K_2S_2O_8$ initiation	
		25°C	40°C	50°C	40°C	50°C
γ -Ray prepared latex	1.6×10^{15}	1.3×10^{15a}	5.4×10^{15a}	1.3×10^{15a}	0.57×10^{15a}	2.9×10^{15a}
	29	-	-	-	-	-
	34	-	-	73	8.7	23
	29	-	-	-	-	-
SR-5937 latex	3.2×10^{14}	21	23	41	40	69
	6.6	20	-	25	22	39

^aThe rate of radical formation in aqueous phase/sec ml H_2O .

charged is dissolved in the polybutadiene particles. This assumption, however, may not be correct. The diffusion of monomer from monomer droplets to polymer particles becomes slower and slower as the monomer droplets become smaller and the monomer concentration in the polymer particles approaches the saturation value. Probably it will take a long time in this case for the polymer particles to be saturated with monomer. While in the γ -ray-induced systems the ampoules were stored overnight before irradiation to saturate the polymer particles with monomer, in the chemical initiator systems polymerizations started after 1-2 hr storage with frequent and rigorous agitation. Thus the smaller values of k_p observed for the experimental runs of the higher particle concentration may result from the overestimation of the value of $[M]$.

The activation energy was calculated from the temperature dependence of k_p . As shown in Table 3, the values, except that for the γ -ray-prepared latex- $K_2S_2O_8$ system, are in good agreement with reported values; 7.8 kcal/mole by Matheson et al. [8], 7.4-8.4 kcal/mole by Morton et al. [5, 6] and 11.7 kcal/mole by Smith [3]. The unusually high activation energy observed for the

TABLE 3. Calculated Values of Activation Energy (in kcal/mole) for the Propagation Reaction of Styrene

	γ -Ray initiation	$K_2S_2O_8$ initiation
γ -Ray prepared latex	9.4	19.5
SR-5937 latex	8.3	11.0

γ -ray latex- $K_2S_2O_8$ system seems to arise from the low value of k_p observed at 40°C, which may be explained by the transfer of the radicals out of the particles. The decomposition of $K_2S_2O_8$ is quite slow at this temperature, and the number of radicals produced is very low compared with the number of the particles. Consequently, the time interval between the entrances of two radicals into a polymer particle becomes so long that the radicals in the particle have many chances to transfer to monomer molecules and probably the chance to transfer out of the particle. This situation leads to a lower

radical number than one half of the number of the polymer particles, which is assumed in the Smith-Ewart theory to be equal to the radical number.

The grafting efficiency, i.e., the fraction of grafted styrene to the total amount of styrene polymerized, was calculated from the extraction data according to

$$Gr = \frac{T(1 - s) - B(1 - x)}{S} \quad (2)$$

where S stands for the total amount of styrene polymerized, B for the amount of base polybutadiene, T for the amount of crude polymer, s for the fraction of the crude polymer soluble in cold methyl ethyl ketone, and x for the correction factor for the small solubility of polybutadiene in methyl ethyl ketone.

In Fig. 7 the values of Gr are plotted vs the polymerization conversions under the various conditions for the γ -ray-prepared latex systems. In Figs. 8 and 9 the same plots are given for the SR-5937 latex systems. Though the points are somewhat scattered in all cases, it is a common trend that the values of Gr decrease with increasing conversion. In the γ -ray-prepared latex systems Gr ranges from 30 to 60%, while it is smaller in the SR-5937

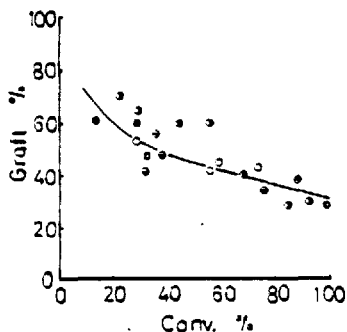


FIG. 7. Plot of the grafting per cent vs conversions for γ -ray-prepared latex systems. (\odot) γ -ray initiation, 25°C, $N = 6.7 \times 10^{15}/\text{ml H}_2\text{O}$. (\circ) γ -ray initiation, 25°C, $N = 3.2 \times 10^{15}/\text{ml H}_2\text{O}$. (\ominus) γ -ray initiation, 40°C, $N = 3.2 \times 10^{15}/\text{ml H}_2\text{O}$. (\oplus) $\text{K}_2\text{S}_2\text{O}_8$ initiation, 40°C, $N = 3.2 \times 10^{15}/\text{ml H}_2\text{O}$. ($\omin�$) $\text{K}_2\text{S}_2\text{O}_8$ initiation, 50°C, $N = 3.2 \times 10^{15}/\text{ml H}_2\text{O}$.

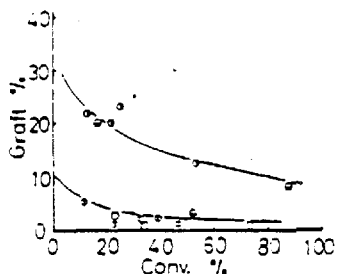


FIG. 8. Plot of the grafting per cent vs conversions for SR-5937 latex systems with γ -ray initiation. (●) 25°C, $N = 6.6 \times 10^{14}$, ml H_2O . (⊕) 25°C, $N = 3.2 \times 10^{14}$, ml H_2O . (⊖) 40°C, $N = 6.6 \times 10^{14}$, ml H_2O . (○) 40°C, $N = 3.2 \times 10^{14}$, ml H_2O .

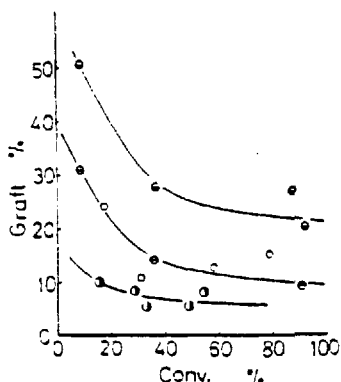


FIG. 9. Plot of the grafting per cent vs conversions for SR-5937 latex systems with $K_2S_2O_8$ initiation. (⊖) 40°C, $N = 6.6 \times 10^{14}$, ml H_2O . (⊕) 40°C, $N = 3.2 \times 10^{14}$, ml H_2O . (○) 50°C, $N = 6.6 \times 10^{14}$, ml H_2O . (●) 50°C, $N = 3.2 \times 10^{14}$, ml H_2O .

latex systems. It is of interest to note that in Figs. 8 and 9 Gr is always higher in the higher particle number systems than in the lower particle number systems, if the other conditions are the same. Moreover, no tendency was observed of the radiation initiation having an advantage over the chemical initiation in regard to grafting efficiency.

However, as will be shown later, the higher radical fluxes readily obtainable with radiation initiation appear to lead to a larger number

of shorter grafted side chains. This could be of great advantage in subsequent applications.

The molecular weights of extracted polystyrene measured by viscometry are listed in Table 4 compared with those calculated theoretically using the equations

$$P_{no} = k_p [M] \frac{N}{R} \quad (3)$$

$$\frac{1}{P_n} = \frac{1}{P_{no}} + \frac{k_{trm}}{k_p} \quad (4)$$

where R is the rate of the radical formation per milliliter of water and k_{trm} is the rate constant of chain transfer to monomer.

Generally, the agreement between the experimental results and the theoretical predictions is rather good for the radiation-induced systems. On the other hand, in the case of the chemical initiator systems the experimental values are smaller than the theoretical ones, even if the chain transfer reaction is taken into account. This may be due partly to the actually smaller values of $[M]$ as mentioned before and partly to the radical transfer out of the polymer particles.

A simple model of the grafting reaction is considered in order to elucidate the reaction mechanism and to explain some aspects of the experimental results. It is assumed that the Smith-Ewart theory is applicable to the present systems. Thus all radicals formed exclusively in the aqueous phase enter the polymer particles, and the polymerization takes place only in the polymer particles. Immediately after entering a particle, a radical starts the polymerization reaction as a propagating radical and continues the reaction until it terminates its life through an essentially instantaneous reaction with the next radical entering the particle. The lifetime of a propagating radical is decided by the ratio of the polymer particle number to the rate of radical formation, and during the lifetime a propagating radical has only two possibilities: reactions with the double bonds in monomer (Reaction 7) and reaction with the double bonds in polybutadiene (Reaction 5). There may be another possible reaction such as chain transfer reaction to polybutadiene molecule (3'). However, this is not so important a problem. If Eq. (8) is meant to include not only the

TABLE 4. Molecular Weights ($\times 10^{-5}$) of Extracted Polystyrene

	Particle No./ ml H ₂ O	Polymerization conditions					
		γ-Ray initiation			K ₂ S ₂ O ₈ initiation		
		25°C	40°C	40°C	40°C	50°C	50°C
		1.3×10^{14a}	1.3×10^{14a}	0.57×10^{13a}	0.57×10^{13a}	2.9×10^{13a}	
γ-Ray prepared latex	1.6×10^{15}	obs	3.5	-	-	-	-
		calc ^b	4.4				
		calc ^c	3.9				
	3.2×10^{16}	obs	10	9.0	6.5	7.0	
		calc ^b	8.0	14	330	96	
		calc ^c	6.5	10	31	25	
	6.7×10^{16}	obs	11	-	-	-	
		calc ^b	16				
		calc ^c	11				
SR-5937 latex	3.2×10^{14}	obs	1.2	2.0	6.6	6.8	
		calc ^b	0.8	1.4	33	9.6	
		calc ^c	0.8	1.4	17	7.4	
	6.6×10^{14}	obs	1.4	2.5	11	4.0	
		calc ^b	1.7	3.0	78	20	
		calc ^c	1.6	2.7	24	13	

^aRate of radical formation in aqueous phase/sec ml H₂O.^bCalculated according to Eq. (3).^cCalculated according to Eq. (4).

addition reaction but also the chain transfer reaction to polybutadiene, the model is rather easy to deal with by using only Eqs. (5)-(10).



where W refers to a water molecule, R to an initiating radical, P to a propagating radical, and k_p and k_q refer to the rate constants of the corresponding reactions.

If p and q are defined as the probabilities of the reaction of a propagating radical with monomer (propagation process) and of the reaction with polybutadiene (grafting process), respectively, then

$$p + q = 1 \quad (11)$$

The probability g by which a radical entering a polymer particle reacts with polybutadiene one or more times during its lifetime according to the Eq. (8) is expressed as

$$g = 1 - p^n \quad (12)$$

where n is the number of the repeating propagation and grafting processes which one radical experiences during its lifetime,

corresponding to the kinetic chain length or the number-average degree of polymerization of the polystyrene chain. It is easily shown that the grafting efficiency, Gr is equal to the probability g .

$$Gr = g = 1 - p^n \quad (13)$$

Remembering that $0 < p < 1$, the above expression leads to the important conclusion that the grafting efficiency increases with increasing n , that is, increasing degree of polymerization of the polystyrene chain. This seems to explain one aspect of the experimental results satisfactorily. The time interval between the entrances of two successive radicals into a polymer particle increases with increasing particle number if the rate of the radical formation is constant. Hence the grafting efficiency is higher in the systems with the larger number of the particles if other conditions are the same.

The probability q is expressed using the rate constants k_p and k_q as follows.

$$q = \frac{k_q(PB)}{k_p(M) + k_q(PB)} \quad (14)$$

where (PB) is the concentration of the reaction sites of polybutadiene in the particles. Usually the first term in the denominator is much larger than the second term. Then q is given approximately by

$$q = \frac{k_q(PB)}{k_p(M)} \quad (15)$$

As the reaction proceeds, (PB) decreases in two ways, that is, by the dilution of polybutadiene with formed polystyrene and associated styrene monomer, and by the consumption of the reaction sites, the former being much more predominant. It follows that q and, consequently, Gr decrease with increasing conversion, as already seen in Figs. 7-9.

The foregoing discussion is based on the assumption that all radicals are formed exclusively in the aqueous phase. In the case

of the radiation initiation, however, radicals are also produced on polybutadiene molecules through the direct interaction of radiation with polybutadiene, though the number of such radicals is ordinarily very small in comparison with the number of radicals produced in the aqueous phase. The radicals formed on polybutadiene can possibly make a contribution to the grafting process. Therefore, if the rate of radical formation on polybutadiene is not negligible compared with the rate of radical entrance into a particle, then a higher grafting efficiency is expected for the γ -ray initiation than for the chemical initiation. As already described, no tendency of the radiation initiation increasing the grafting efficiency was observed. On the contrary, it apparently reduces the grafting efficiency in some cases. However, it should be noted that in the chemically initiated systems the lifetime of propagating radicals is quite long on account of the low decomposition rate of the initiator at these temperatures. The apparent high grafting efficiencies may be attributed to the long lifetime of the propagating radicals.

In Table 5 are shown the values of the parameter q' calculated according to Eqs. (17) and (18) with the use of the measured degrees of polymerization.

$$\log p = \frac{1}{n} \log(1 - Gr) \quad (16)$$

$$\log p' = \frac{1}{p} \log(1 - Gr) \quad (17)$$

$$q' = 1 - p' \quad (18)$$

In order to find out whether the radicals formed on polybutadiene make an important contribution to the grafting process, it is essential to exclude the effect of molecular weight of polystyrene chains on the grafting efficiency, and the parameter q' seems to be suitable for this purpose. In Table 5 no appreciable difference is seen between the q' values in the γ -ray initiation and the chemical initiation, which means that under the present experimental conditions the number of radicals produced on polybutadiene by the direct interaction of radiation is negligibly small compared with the number of radicals entering the particles from the aqueous phase.

TABLE 5. The Values of Parameter q' ($\times 10^5$)

	Particle No./ml H ₂ O	Polymerization conditions					
		γ -Ray initiation		K ₂ S ₂ O ₈ initiation		50°C	
		25°C	40°C	40°C	40°C		
γ -Ray prepared latex	3.2×10^{15}	10	16	15	18		
	6.7	12	-	-	-		
SIR-5937 latex	3.2×10^{14}	4	3	6	1		
	6.6	21	12	7	9		

The consideration of G-values of radical formation makes the situation clearer. The G-value of radical formation in the aqueous phase is assumed to be 6 in this work, and the ratio of polybutadiene to water was taken to be about 1/12 in most of the experimental runs. If the G-value of radical formation on polybutadiene is assumed to be about 1, the rate of radical entrance from the aqueous phase to the particles is about 70 times as large as the rate of radical formation on polybutadiene.

As indicated in Table 5, the parameter q' is approximately of the order of 10^{-4} . As (M) was taken to be at most 10 times as large as (PB) , k_p/k_q is estimated to be nearly of the order of 10^{-3} .

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