Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Sundardi, F. and Zubir, A.(1985) 'Radiation Emulsion Polymerization of n-Butyl Acrylate, Glycidyl Methacrylate, and Methacrylic Acid', Journal of Macromolecular Science, Part A, 22: 12, 1647 — 1657
To link to this Article: DOI: 10.1080/00222338508063362
URL: http://dx.doi.org/10.1080/00222338508063362

J. MACROMOL. SCI.–CHEM., A22(12), pp. 1647-1657 (1985)

Radiation Emulsion Polymerization of n-Butyl Acrylate, Glycidyl Methacrylate, and Methacrylic Acid

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ABSTRACT

The rate of emulsion polymerization of N-butyl acrylate and glycidyl methacrylate is influenced by the irradiation dose rate and the emulsifier type. With regard to the rate of polymerization and the stability of polymer emulsion, sodium dodecyl benzene sulfonate (SDBS) is found to be a better emulsifier than Tween 20. Irradiation dose, in order to obtain 90% conversion, is about 50 krd using SDBS emulsifier, compared to about 160 krd using Tween 20 emulsifier, both with an irradiation dose rate of about 80 krd/h. Irradiation dose, in order to obtain the same conversion, decreases with a decrease in irradiation dose rate. Thermal analysis showed that the glycidyl methacrylate content greatly influences the thermal stability of the polymer film.

INTRODUCTION

The mechanism of emulsion polymerization reaction which is now generally accepted is based on work by Harkins et al. [1]. The simple description of rate theory was first given by Smith and Ewart [2], and will be referred to as the Smith-Ewart rate theory. The general equa-

 0022-233X/85/2212-1647$3.50/0

tion applicable to solution, bulk, suspension, and emulsion can be written as

$$R_p = \frac{\bar{n}}{N_A v} k_p[M] \tag{1}$$

where R_p = rate of propagation or polymerization
$\bar{n}$ = average number of radicals in volume v
N_A = Avogadro number
k_p = propagation rate constant
$[M]$ = monomer concentration

According to the Smith-Ewart rate theory [3], for ideal emulsion polymerization the average number of radicals $\bar{n}$ in one polymer particle is 0.5, and hence the rate of polymerization can be written

$$R_p = Nk_p[M]/2N_A \tag{2}$$

where N = total number of particles per liter of organic phase.

The total number of particles N depends on several factors, such as the rate of radical production, the rate of volume increase of a particle, the area occupied by one soap molecule, and the amount of soap present. This relation can be written as follows [3]:

$$N = 0.37(\rho/\mu)^{2/5}(aS)^{3/5} \tag{3}$$

where ρ = rate of radical production
μ = rate of volume increase of a particle
a = area occupied by one soap molecule
S = amount of soap present

The theoretical prediction contained in Eq. (3) has been tested by a number by authors, mostly by Bartholome et al. [4]. It was found that the number of particles formed was proportional to the 2/5 power of the amount of initiator.

The rate of emulsion polymerization is largely influenced by the rate of radical production, the amount of soap, and the type of soap used as emulsifier. This paper presents the influence of the type of soap and the irradiation dose rate of emulsion polymerization of a mixture of N-butyl acrylate, glycidyl methacrylate, and methacrylic acid, initiated by gamma irradiation.

A mixture of N-butyl acrylate, glycidyl methacrylate, and methacrylic acid contains a large amount of components which are soluble in water. Thus, the mechanism of emulsion polymerization as stated by Harkin et al. cannot be applied perfectly. In this situation the polymer particles cannot be expected to originate solely from the monomer soluble in micelles but partly from the polymer molecule precipitated in water. It can be understood that the polymerization rate, the number of polymer particles, and the emulsion stability are greatly influenced by the rate of agitation and the stability properties of the emulsifier. For this reason it is concluded that an ideal emulsion polymerization such as stated by Smith and Ewart cannot be attained. Experimental results showed significant deviation from the Smith-Ewart rate theory for emulsion polymerization of monomers that are highly soluble in water, such as vinyl acetate [6, 7].

Extensive studies on the radiation emulsion polymerization of vinyl monomers had been carried out by Hummel et al. [8]. It has been reported that the number of particles is approximately proportional to the 0.15 power of the irradiation dose rate, which indicates a small deviation from the Smith-Ewart rate theory.

EXPERIMENTAL

Materials

Monomers such as N-butyl acrylate, glycidyl methacrylate, and methacrylic acid were purified by distillation under reduced pressure. Other chemicals such as polyxyethylene sorbitanmonolaurate (Tween 20), sodium dodecile benzene sulfonate (SDBS), and sodium sulfite were of analytical grade and used without further purification. The hydrophylic-lipophylic balance (HLB) value of Tween 20 emulsifier is about 16.7 [9].

Equipment and Method

Irradiation was carried out in a Panoramic Co-60 irradiator of 55 kCi activity. The irradiation dose rate was calibrated using a Perspect dosimeter.

Emulsion of monomers was achieved by agitating a mixture of monomers and water in a close vessel. This emulsion was then irradiated in an agitated vessel. Conversion was determined gravimetrically by precipitating the polymer particles from the water phase.

A Shimadzu thermal analyzer DT 30 was used to determine the thermal stability of polymer. The activation energy for thermal degradation was determined by measuring the displacement of an exotherm

peak with an increase of the heating rate. A general equation was deduced for such a method:

$$\log \beta = -0.457E_a(1/T_m)/R \quad (4)$$

where β is the heating rate, 0.457 is a factor obtained from mathematical deduction, R is the universal gas constant, E_a is the activation energy, and T_m is the peak temperature (°K). By plotting log β against $1/T_m$, a straight line is obtained whose slope is proportional to E_a [5].

RESULTS AND DISCUSSION

Influence of Agitation and Flowing of N_2 during Irradiation

Table 1 shows that emulsion polymerization conversion obtained by agitation during irradiation is much lower than conversion obtained by nitrogen flow during irradiation. This may be due to the effect of oxy-

TABLE 1. Radiation Polymerization of N-Butyl Acrylate Emulsion with Composition as Follows:

N-Butyl acrylate	98
Glycidyl methacrylate	6
Tween 20	5
Water	245

Irradiation, dose, krd	Conversion, % I	II	III	Remarks
80	77.6	5.4	49.4	Irradiation dose rate: 80 krd/h.
160	78.4	5.5	46.8	Emulsion was stable before irradiation:
240	75.8	5.4	45.8	
320	76.5	5.5	40.1	I. N_2 flow during irradiation
400	77.3	5.0	43.2	II. Agitation during irradiation
440	89.9	8.5	41.3	III. Without agitation and N_2 flow

TABLE 2. Radiation Polymerization of N-Butyl Acrylate Emulsion with Composition as Follows:

N-Butyl acrylate	98
Glycidyl methacrylate	6
Methacrylic acid	1
Tween 20	3
Water	245

Irradiation dose, krd	Conversion, %	Remarks
40	3.79	Irradiation was carried out in a closed vessel agitated with a magnetic stirrer. Irradiation dose rate: 80 krd/h. Small coagulation after irradiation
80	13.55	
120	16.46	
160	17.46	
200	17.46	

gen dissolved in water which behaves as a radical scavenger. The contact of liquid with air increases with an increase in agitation, and so the oxygen content in the liquid increases with an increase in agitation. In the case of no agitation during irradiation, contact of the liquid with air is limited, and hence it is expected there will be higher conversion than what is obtained by agitation during irradiation. The addition of a small amount of sodium sulfite into the emulsion reduces the amount of dissolved oxygen, and hence the rate of polymerization can be expected to increase. Tables 2, 3, and 4 show the influence of the addition of sodium sulfite into butyl acrylate emulsion on the rate of polymerization. It is seen that the conversion of emulsion polymerization obtained by the addition of sodium sulfite is much higher than that carried out without sodium sulfite under the same condition.

Experimental results showed that the polymer emulsion prepared by irradiation is unstable. Butyl acrylate and glycidyl methacrylate are slightly soluble in water, but methacrylic acid is highly soluble in water. Therefore, a large amount of monomers is soluble in water, and hence the polymer particles which are formed by radiation do not come from the soap micelles, as stated in the Harkin's conception, but from the precipitation of polymer molecules formed in the water phase. These precipitated polymer molecules behave as seed particles for further polymerization reaction in which the stability of the polymer emulsion is strongly influenced by agitation and the emulsifier content.

TABLE 3. Radiation Polymerization of N-Butyl Acrylate Emulsion with Compositions as Follows:

	I	II	III
N-Butyl acrylate	98	98	98
Glycidyl methacrylate	6	4	2
Methacrylic acid	2	2	2
Tween 20	4.24	4.16	4.08
Na_2SO_3	0.16	0.15	0.14
Water	245	245	245

Irradiation dose, krd	Conversion, % I	II	III	Remarks
13.3	9.98	10.53	9.93	N_2 gas flowed into emulsion for about 10 min
26.7	12.40	15.56	15.69	Irradiation: in a closed vessel with a magnetic stirrer
40.0	15.49	25.04	28.05	Irradiation dose rate: 80 krd/h
53.3	59.27	33.58	48.46	Emulsion was unstable after irradiation
66.7	73.06	82.17	41.64	
80.0	91.65	96.00	72.94	

Influence of Emulsifier

Ionic emulsifiers such as SDBS are better emulsifiers than Tween 20 with regard to the rate of polymerization and polymer emulsion stability. This can be seen in Table 5. In order to obtain 98% conversion when using SDBS as the emulsifier, an irradiation dose of about 26.4 krd was needed as compared to about 180 krd when using Tween 20 as the emulsifier. The emulsion prepared using SDBS as the emulsifier was unstable before irradiation but quite stable after irradiation. This may be due to the ionic character of the hydrophilic group in SDBS which acts as a repulsive power between particles. The influence of a small amount of sodium sulfite on the rate of conversion is not clear if N_2 flows before irradiation.

Influence of Irradiation Dose Rate

Table 6 shows the influence of the irradiation dose rate on conversion. The irradiation dose needed to obtain the same amount of conversion is lower at lower irradiation dose rates. In general,

TABLE 4. Radiation Emulsion Polymerization of N-Butyl Acrylate with Compositions as Follows:

	I	II
N-Butyl acrylate	98	98
Methacrylic acid	2	1
Glycidyl methacrylate	6	6
Tween 20	5.3	5.25
Na_2SO_3	0.53	0.26
Water	245	245

Irradiation dose, krd	Conversion, % I	Conversion, % II	Remarks
40	21.16	5.34	Irradiation in a closed vessel with a magnetic stirrer
80	25.35	19.32	Irradiation dose rate: 80 krd/h
100	-	20.23	Irradiation emulsion stable up to 3 days
120	29.72	38.12	Emulsion was stable before irradiation
140	-	78.40	
160	73.82	92.20	
180	94.15	99.33	
193	-	99.20	

these results are not in agreement with the Smith-Ewart rate theory. In solution polymerization the irradiation dose needed to obtain a given amount of conversion is proportional to the 0.5 power of the irradiation dose rate [10]. In emulsion polymerization the irradiation dose needed to obtain a given amount of conversion is proportional to the 0.6 power of the irradiation dose rate. Table 6 shows that in order to obtain approximately 80% conversion, the irradiation dose needed is proportional to the 0.67 power of the irradiation dose rate. This result is not exactly in agreement with solution or emulsion polymerization rate theory.

Thermal Stability

Figures 1, 2, and 3 show the thermogram peaks of polymers with different compositions prepared by radiation. Activation energy E_a for degradation calculated using Eq. (4) shows that E_a increases with

TABLE 5. Radiation Emulsion Polymerization of N-Butyl Acrylate with Composition as Follows:

	I	II
N-Butyl acrylate	98	98
Glycidyl methacrylate	6	6
Methacrylic acid	2	2
SDBS	5	5
Na_2SO_3	-	0.26
Water	245	245

Irradiation dose, krd	Conversion, % I	Conversion, % II	Remarks
13.7	-	71.21	Irradiation in a closed vessel with a magnetic stirrer
26.4	-	98.96	N_2 flow before irradiation
40.0	96.9	99.07	Irradiation dose rate: 80 krd/h
53.3	-	99.27	Emulsion was stable before and after irradiation
66.7	-	99.33	
80.0	97.7	99.72	
100.0	97.8	-	
120.0	97.9	-	

a decrease in the glycidyl methacrylate content in polymer. This may be due to the lower thermal stability of glycidyl methacrylate compared to butyl acrylate. This means that the addition of glycidyl methacrylate in N-butyl acrylate emulsion has a negative effect on polymer thermal stability.

Film Properties

A clear and coherent film is obtained by evaporating the polymer emulsion on a flat glass, which shows that this emulsion has the potential for use as a binding agent for water-borne paint.

CONCLUSION

An emulsion of N-butyl acrylate, glycidyl methacrylate, and methacrylic acid monomers can easily be polymerized by gamma irradiation.

TABLE 6. Radiation Emulsion Polymerization of N-Butyl Acrylate with Composition as Follows:

N-Butyl acrylate	98
Glycidyl methacrylate	6
Methacrylic acid	2
SDBS	5
Na_2SO_3	0.26
Water	245

Irradiation dose, krd	Conversion, % I	II	III	IV	Remarks
6.7	57.72	53.06	19.45	42.86	N_2 flow before irradiation
13.4	60.22	61.18	27.04	77.78	Agitation during irradiation
20.0	65.90	67.90	41.04	95.70	Emulsion was stable after irradiation
26.8	69.16	83.65	81.84	95.94	Irradiation dose rate:
33.3	80.69	95.83	93.21	95.54	I = 80 krd/h
40.0	85.19	96.76	94.60	94.22	II = 60 krd/h III = 40 krd/h IV = 20 krd/h

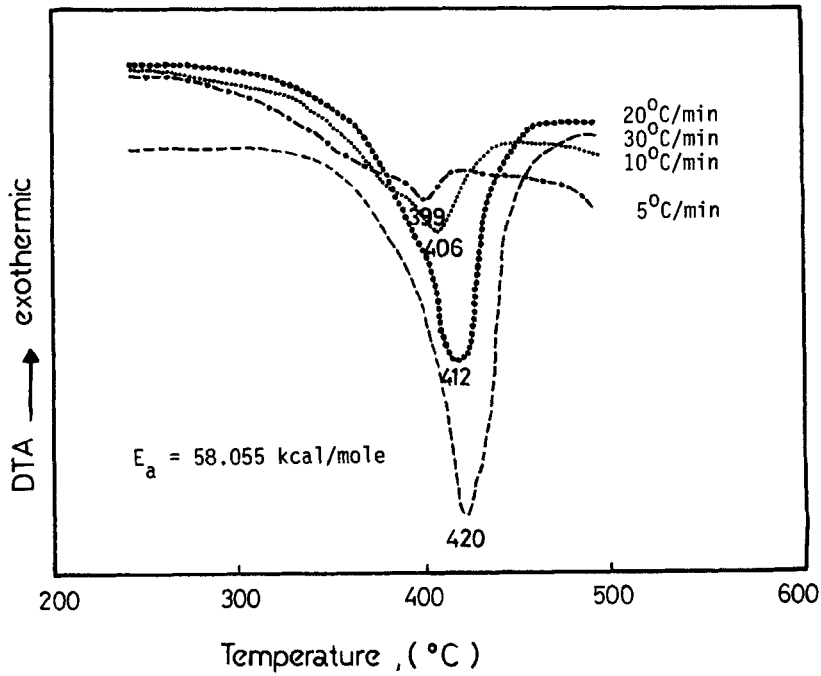

FIG. 1. Thermogram of a polymer prepared by radiation emulsion polymerization. Monomer composition: N-butyl acrylate, 98; glycidyl methacrylate, 2; methacrylic acid, 2.

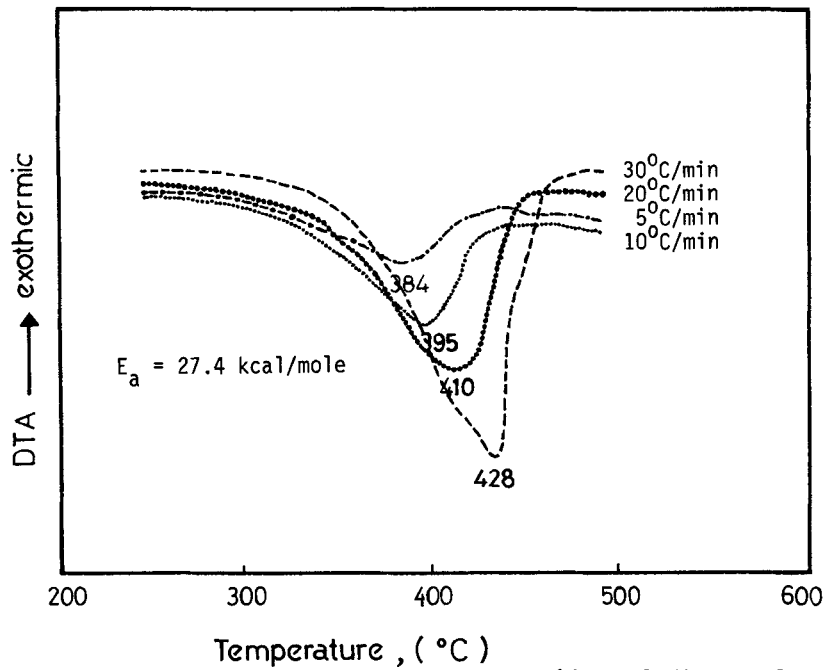

FIG. 2. Thermogram of a polymer prepared by radiation emulsion polymerization. Monomer composition: N-butyl acrylate, 98; glycidyl methacrylate, 4; methacrylic acid, 2.

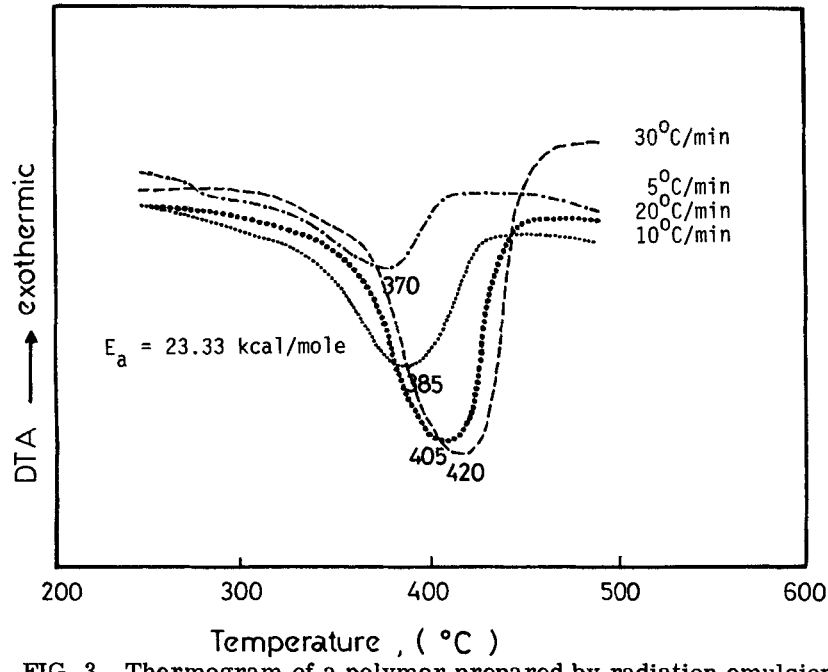

FIG. 3. Thermogram of a polymer prepared by radiation emulsion polymerization. Monomer composition: N-butyl acrylate, 98; glycidyl methacrylate, 6; methacrylic acid, 2.

An irradiation dose of less than 20 krd can yields polymer conversion of more than 90% under the best condition. The polymer emulsion was stable for more than 4 weeks and yielded a clear, coherent film.

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Accepted by editor July 27, 1984
Received for publication August 13, 1984