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Emulsion polymerization of 2-hydroxyethyl methacrylate and partition of monomer between particles and water phase

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SUMMARY

Using sodium dodecyl sulfate (SDS) as the single surfactant 2- hydroxyethyl methacrylate (HEMA, extremely water-soluble) was polymerized at 60°C in aqueous medium to obtain latexes with average particle diameter below 80 nm and the extrapolated k_p value was estimated to be 200±20 (L/mol-s). Values of monomer concentration in particles ([M]) used in this calculation were obtained by interpolating the literature available partition data of HEMA between the gel phase (i.e., poly(2-hydroxyethyl methacrylate) and the water phase. The [M] values (< 1.00 mol/L) are much lower than those for the sparely-soluble monomer (3 to 4 mol/L), and the [M] values decrease with increasing conversion.

INTRODUCTION

It is usually accepted that only monomers with low aqueous (aq.) solubility were used in emulsion polymerization and the latexes prepared can have quite high solid contents. On the contrary, the maximum solid contents which can be attained in emulsion polymerization of certain highly water-soluble monomers are rather limited. For instance, the high bound is about 11 wt.-% for polyacrylonitrile (1) (compared to 50-60 wt.-% for the usual latex systems), where the acrylonitrile has an aq. solubility of 8.5 wt.-% at 50°C (2).

The preparation of homopolymeric poly(2-hydroxyethyl methacrylate) (PHEMA) latex with adequately high solid content is not easy at all compared to the hydrogel preparation, since the monomer exhibits an extremely high aq. solubility (3,4) and the latex faces coagulation easily.

Reports concerning the polymerization of HEMA in aq. medium did not describe homopolymerization (5,6). Other reports mentioned the homopolymerization of HEMA in aq. medium using redox initiator (7-9), or other ways of initiation (10,11), but did not show the particle size data.

A breakthrough was made in this laboratory (3) that in the presence of surfactants, HEMA and hydroxypropyl methacrylate (HPMA) were polymerized separately in aq. medium to obtain polymer latexes with a solid content as high as 10 wt.-%. The polymerization was conducted using a mixture of ionic surfactant (e.g., sodium dodecyl sulfate (SDS)) and colloid (e.g., polyvinyl alcohol, PVA) under a comparatively faster agitation. However, the latex particles prepared had larger diameters (e.g., 120 - 240 nm) than the plain latex particles (e.g., below 100 nm).

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It is possible to evaluate the k_p values for a monomer polymerized through emulsion polymerization by an approach (12,13) stemming from the analysis of Stockmayer (14). In that approach, the (k_p x ñ) value was plotted against the volume-average particle diameter (Dv), and the asymptote leveled-off at the lower end (Dv = 50 - 80nm), where ñ (i.e., average radical number per particle) can be considered as 0.5 and, therefore, the k_p value can be estimated. The detailed explanation for this approach is referred to Ref. 13.

However, there was a restriction on using a single surfactant of SDS in the emulsion polymerization of HEMA, where no conversion was observed for several hours. In this study, the restriction was removed by carefully adjusting the reaction conditions (e.g., keeping the agitation rate low). Besides, the PHEMA latexes prepared by this way have smaller average diameters, suitable for the analysis of the k_p value.

People used to consider that the course of emulsion polymerization proceeds through three intervals (15,16). The particle number increases with time in Interval I, where latex particles are being formed, and then remains constant during Intervals II and III. In Interval II, the monomer concentration in particle ([M]) can be regarded to be constant (17-19). Monomer droplets exist from the beginning of the polymerization until the end of Interval II. The transition from Intervals II to III occurs depending on the type of monomer (15,16). The transition occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles increases (15,20). The fact that HEMA can form homogeneous solution with water in any ratio discloses a totally different situation from what people usually considered before (3). Instead, no more monomer droplets form and [M] values are not longer constants during the emulsion polymerization.

Published reports concerning the AIBN-initiated emulsion polymerization mechanism of HEMA are not available. Other reports (21,22) mentioned AIBN-initiated HEMA polymerizations, but the polymerizations were not conducted in emulsion. Others report (23-26) the emulsion polymerizations of other monomers initiated by oil-soluble initiators, for which two different mechanisms were proposed for the production of radicals: (i) radicals formed in monomer-swollen polymer particles desorb to the continuous phase (23, 24), and (ii) radicals formed in continuous phase dissolve in water (25). It was stressed (26) that radicals located in the polymer particles might be terminated easily.

This report presents how the [M] data varied with conversion for the HEMA system by interpolating the literature data concerning the partition of monomer between the gel phase and the water phase. In addition, we have corrected the latex particle diameters utilizing the volume swelling data of the polymer in both water and a mixture of water and monomer.

EXPERIMENTAL

Materials

HEMA (from TCI, with a minimum purity of 95.0%) was purified by distillation under reduced pressure. Water was from a Reverse Osmosis System (Ultra-pure Water System, Model DI-S3, Kintech Co.) with a conductivity of 2 µmho. Other chemicals were reagent grade and used as received. Sodium dodecyl sulfate (SDS) was from Riedel-de Haen. 2,2'-Azobis-(isobutyronitrile) (AIBN) was from Wako.

Polymerization and latex characterization

Polymerization recipes are shown in Table 1. Polymerizations were conducted at 60°C, in 250 -cm^3 four-neck, round-bottom flasks in a constant temperature bath, with a

mechanical stirring rate of 100 rpm.
The conversion of monomer to polymer was determined gravimetrically, where 2 to 3 cm^3 of the latex was injected into a solution containing 10 cm^3 of methanol (as a coagulation agent) and 10 to 15 drops of a 3 wt-% 4-methoxyphenol-water solution (as a shortstop). The methanol and water were then removed by drying in oven at 80 °C until a constant weight was obtained. (It took about 40 hours or more.) The polymerization rate was determined from the slope of the conversion-time curve in constant rate region. The particle size was determined with a Photal DLS 3000/3100 dynamic light scattering (DLS) spectrophotometer. Note that since the particles are highly swollen, a correction for particle size was made by dividing the linear swelling ratio (l_s/l_0), where l_s is the linear dimension of the swollen sample and l_0 is the corresponding dimension of the dry sample. The $(l_s/l_0)^3$ data at the % conversions of 10, 70 and 100, respectively, are adopted as 2.25, 1.95 and 1.68 for the PHEMA (3). The number-average, volume-average, and weight-average diameters (i.e., D_n, D_v, and D_w, respectively), and the particle number per L of aq. phase or particle concentration (N) are defined as usual (27).

Table 1
Polymerization recipes

	Mass of ingredients (in g)		
Series	A	B	C
HEMA	15.0	15.0	variable
Water	185	185	[a]
AIBN	0.20	variable	0.20
SDS	variable	0.50	0.30

[a] Water amount =(200 –weight of HEMA).

The product of k_p and ñ was calculated using Eq. 1 as follows:

$$R_p = k_p N \tilde{n} [M]/A_v \qquad (1)$$

where R_p is the rate of polymerization, A_v is Avogadro's number, and [M] is the monomer concentration in particles and was computed according to the partition data of monomer between the particles and the water phase.

RESULTS AND DISCUSSION

Stirring rate- sensitive polymerizations

The stirring rate has a great effect on the emulsion polymerizations of HEMA. In the previous report (3), the emulsion polymerization of either HEMA or HPMA was carried out by using a mixture of anionic surfactant (SDS) and colloid (PVA), under a fast agitation (i.e., 240 rpm), where the higher stirring rate favors the stability of the latex. However, the latex was not stable (i.e., forming hydrogel) when the stirring rate was set at a lower level. In the meantime, if a single surfactant of SDS was used instead of the surfactant mixture, no progress in reaction was observed under the stirring rate of 240 rpm.

In a test-run later, using a single surfactant of SDS, however, the polymerization was found flourishing when the agitation was shut down for a while. The lower stirring rate seemed to favor the initiation. Therefore, we set the agitation rate at 100 rpm to facilitate the polymerization.

The aqueous solution polymerization of HEMA, which can be regarded as one of the steps in the homogeneous nucleation, may be suppressed by increasing the stirring rate. But it is not allowed to perform the emulsion polymerization without stirring since it may lead to gel formation.

Table 2
Effect of SDS content on values of polymerization rate (Rp), volume-average diameter (D_v), particle number per L of aq.phase (N) and average radical number per particle (ñ) at 50% conversion for recipe series A

SDS (g)	Rp $\times 10^5$ (mol /L-s)	D_v (nm)	N $\times 10^{-17}$ (1/L)	ñ
0.30	5.0	57	3.4	0.83
0.35	8.0	37	14	0.32
0.40	5.4	45	7.4	0.41
0.50	7.2	46	6.5	0.62

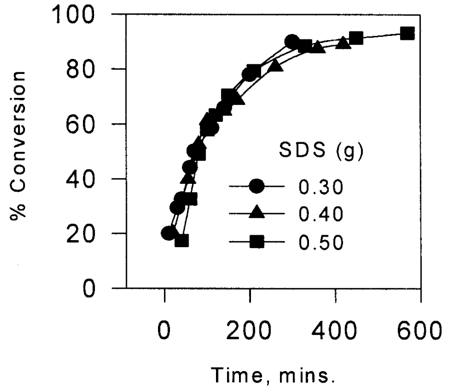

Fig. 1. Conversion-time curves for recipes containing 15.0g of monomer, 185.0g of water, 0.20g of AIBN and various amounts of SDS

Polymerizations using SDS as the sole surfactant

The content of SDS surfactant was ranged from 0.30 to 0.50g in recipe series A (Table 1), where the critical micelle concentration (CMC) is equivalent to 0.47g of SDS in 185g of water.

The polymerization rates do not increase all the way with increasing the SDS content, but show some minor fluctuations with a maximum at 0.35g of SDS, as shown in Table 2. The conversion-time curves are shown in Fig. 1. The particle number per L of aq. phase (N) data show a maximum at the SDS contents below the CMC, as shown in Fig. 2. It may be considered that emulsion polymerization is dominated by the homogeneous nucleation mechanism(28,29), and the initiation is hindered in the presence of micelles when the surfactant concentration is above the CMC.

As the homogeneous nucleation mechanism is concerned, it is elucidated that the initiation takes place in aq. solution, the growing chains precipitate out when they grow to a critical chain length, then a re-dispersion step follows to fulfill the formation of precursor particles. The characteristic behavior was deeply recognized in the preliminary test that the process is sensitive to the contents and types of surfactants, and the stirring rate used, where the higher

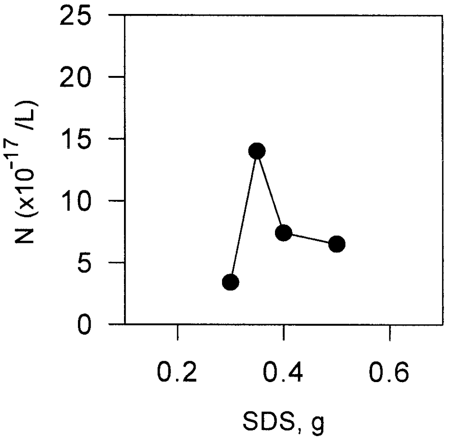

Fig. 2. Much higher nucleation rate occurs when SDS concentrations are lower than the CMC

stirring rate may hinder the chains from precipitating in the precipitation step and thereafter the following step to have nucleation.

Surfactant-free emulsion polymerization (i.e., aqueous solution polymerization) of HEMA showed that the polymerization rate was not negligible if no agitation was applied, and it formed gel easily. However, the polymerization rate was slow when it was conducted with a stirring rate of 100 rpm or higher. On the other hand, in the presence of surfactant (i,e., emulsion polymerization), the polymer chains formed in aqueous phase were precipitated out and might be redispersed again by the help of surfactant molecules, and the polymerization sustained even when the stirring of 100 rpm or higher was applied. Furthermore, it is hard to decide quantitatively the contribution of the aqueous solution polymerization in this case.

Another fact shows that the coagulative mechanism (30-32) also occurs during the emulsion polymerization. As shown in Fig. 3, the particle number per L of aq. phase (N) decreases rapidly at higher conversion (>60%).

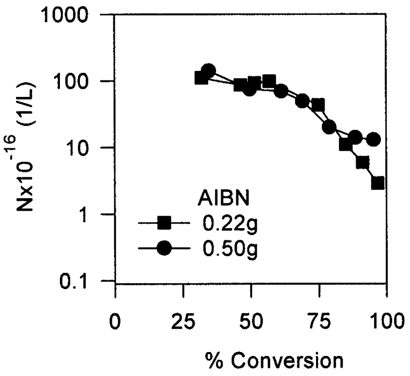

Fig. 3. Particle number per liter of aq. phase (N) versus conversion

Table 3
Effect of AIBN content on values of polymerization rate (Rp), and volume-average diameter (D_v) at 50% conversion for recipe series B

AIBN (g)	Rp $\times 10^5$ (mol/L-s)	D_v (nm)
0.22	9.1	41
0.30	9.3	38
0.40	11	43
0.50	12	44

Effect of AIBN content

It has been pointed out that the use of potassium persulfate (a water-soluble initiator) may lead to either hydrogel formation or no initiation (3).

In this study, an oil soluble initiator (AIBN) was used in emulsion polymerization. Although AIBN is only slightly soluble in water, the polymerization proceeds well. In spite of the limited solubility of AIBN (ca. 0.037 wt.-% in water) (33), the polymerization rate increases slightly with increasing the AIBN content ([AIBN]). However, with increasing the [AIBN], the average particle diameter decreases slightly at first until [AIBN]= 0.30g and then increases again, as shown in Table 3. The degree of data fluctuation for particle diameter is somewhat within the error range.

Partition of monomer between the particles and the water phase

Data for the partition of HEMA between the gel phase and the water phase have been presented elsewhere (4). In this study, those data were interpolated and recalculated to obtain data for monomer concentration in particles ([M]) corresponding to different conversions for various recipes, as shown in Table 4.

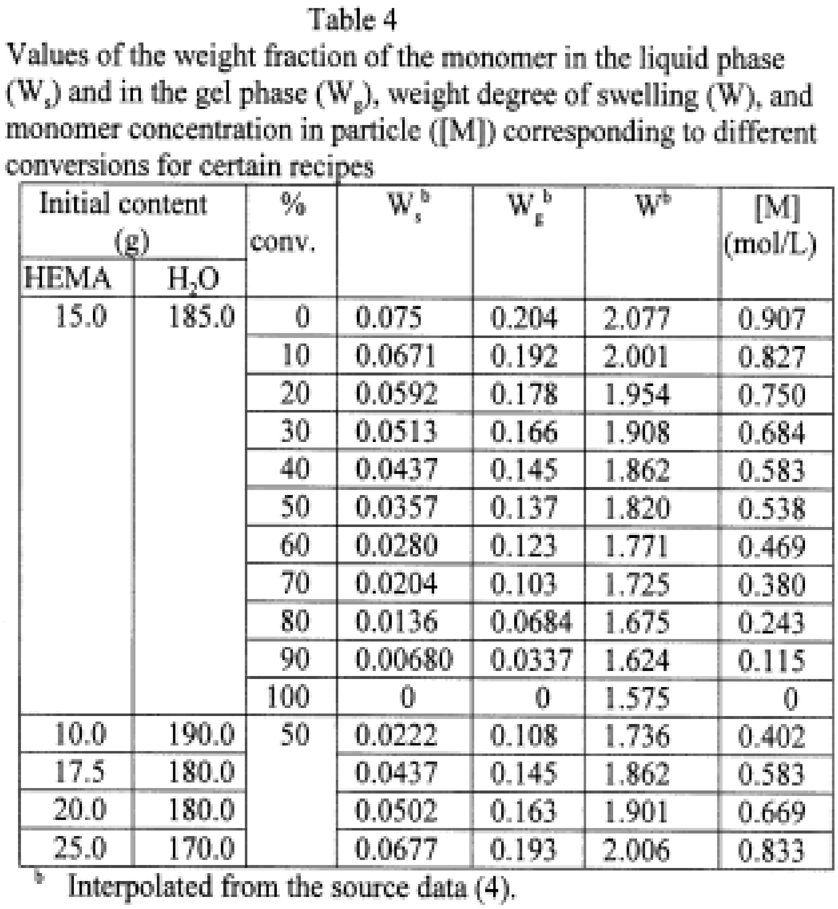

Table 4

Values of the weight fraction of the monomer in the liquid phase (W_s) and in the gel phase (W_g), weight degree of swelling (W), and monomer concentration in particle ([M]) corresponding to different conversions for certain recipes

Initial content (g)		% conv.	W_s^b	W_g^b	W^b	[M] (mol/L)
HEMA	H_2O					
15.0	185.0	0	0.075	0.204	2.077	0.907
		10	0.0671	0.192	2.001	0.827
		20	0.0592	0.178	1.954	0.750
		30	0.0513	0.166	1.908	0.684
		40	0.0437	0.145	1.862	0.583
		50	0.0357	0.137	1.820	0.538
		60	0.0280	0.123	1.771	0.469
		70	0.0204	0.103	1.725	0.380
		80	0.0136	0.0684	1.675	0.243
		90	0.00680	0.0337	1.624	0.115
		100	0	0	1.575	0
10.0	190.0	50	0.0222	0.108	1.736	0.402
17.5	180.0		0.0437	0.145	1.862	0.583
20.0	180.0		0.0502	0.163	1.901	0.669
25.0	170.0		0.0677	0.193	2.006	0.833

[b] Interpolated from the source data (4).

It is interesting to note that the [M] values are much lower than those for the sparely-soluble monomers (e.g., 3 to 4 mol/L), and the [M] values decrease with increasing conversion. The highly swelling nature of the polymer (PHEMA) in water might intrigue erroneous guess to a much higher expected value, and this was proved to be wrong according to our calculation.

Variation of (k_p x ñ) with particle size

The propagation rate constant (k_p) for HEMA is not available in literature. It is possible to obtain the k_p value of HEMA by using the approach (12,13) stemming from the analysis of Stockmayer (14), but attaining latexes with average particle diameter located between 50 and 80 nm is a must. This was fulfilled in this study.

The products of k_p and ñ are plotted against the volume-average particle diameter (D_v), and the curve decreases with decreasing the D_v value, as shown in Fig. 4. Note that the particle diameter data have been corrected by modifying with the swelling data of the polymer in water (or in medium consisting of water and monomer). The details are mentioned in the experimental part. Recipes containing surfactant mixtures (i.e., SDS + PVA) have higher values in both D_v and (k_p x ñ), as we found in this laboratory (Table 5)(34). In this study, we focus on the lower end. The curve levels-off at D_v 's in the range between 50 and 80 nm, where the (k_p x ñ) product reaches a constant value and ñ can be assumed 0.5. The product was estimated to be 100±10 (L/mol-s) and the k_p value is, therefore, 200±20 (L/mol-s).

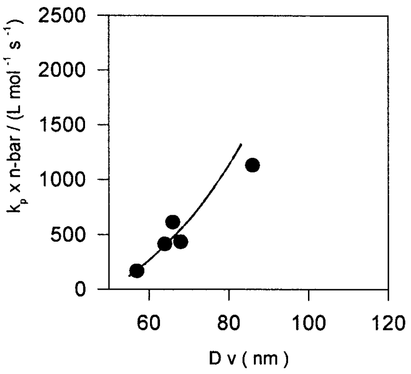

Fig. 4. The value of (k_p x ñ) versus the average diameter (Dv) at 50% conversion for recipe series C

Table 5
Data^c for HEMA emulsion polymerization conducted at 50℃

SDS,g	PVA, g	D_v (nm), at 50% conv.	(k_p x ñ), (L/mol-s)
0.3	0.5^d	60.2	1,190
0.3	1.0^d	87.1	2,590
0.3	1.5^d	143	11,300
0.3	0.5^e	85.1	2,870
0.3	1.0^e	97.0	2,410
0.3	1.5^e	117	4,480

^{c}Data adopted from Ref. 34.
^{d}PVA with MW of 15,000.
^{e}PVA with MW of 72,000.

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REFERENCES

1. Piirma I, Chang JC, Doneshvar M (1985) Polym Prepr (Am Chem Soc) 26(1): 219
2. Lindemann MK (1967), In: Ham GE (ed) Vinyl Polymerization, Dekker, New York (vol. 1, pt. I, pp 260)
3. Chu H-H, Fu D-C (1998) Macromol Rapid Commun 19: 107-110
4. Wichterle O (1971), In: Mark HF, Gaylord NG, Bikales NM (ed) Encyclopedia of Polymer Science and Technology, Wiley, New York (vol. 15, pp 273)
5. Kamei S, Okubo M, Matsumoto T (1986) J Polym Sci, Polym Chem Ed 24: 3109
6. Chen SA, Chang HS (1990) J Polym Sci, Polym Chem Ed 28:2547
7. Macret M, Hild G (1982) Polymer 23: 81
8. Lavro NA, Bondarenko VM, Nikolaev AF (1984) Zh. Prikl Khim (Leningrad) 57(3): 610; Chem Abstr (1984) 101: 38890

9. Lavro NA (1984) Khim Teknol Svoistva i Primenennie Plastmass L pp 17 ; Chem Abstr (1986) 104: 69184w
10. Chang M, Colvin M, Rembaum A (1986) J Polym Sci, Polym Lett Ed, 24: 603
11. Mathew J, Mahadevan V (1995) J PolymSci, Polym Chem Ed.33: 2803
12. Kincaid S (1982) Ph.D. Dissertation, The University of Akron
13. Chu H-H, Gau H-H (1995) Macromol Chem Phys 196: 2251-2258
14. Stockmayer WH (1957) J Polym Sci 24: 314
15. Gardon JL (1977) Emulsion Polymerization, Ch 6 in: Schildknecht CE, Skeist I (ed) Polymerization Process, Wiley New York
16. Odian G (1991) Principles of Polymerization, Ch. 4, 3rd Ed, Wiley New York
17. Weerts PA, German AL, Gilbert RG (1991) Macromol 24: 1622
18. Gerrens H, Kohnlein E (1960) Z Elektrochem 64:1199
19. Gerrens H (1959) Fortschr Hochpolym Forsch 1: 234
20. Ugelstad J, Hansen FK (1976) Rubber Chem Technol 49: 536
21. Arica MY, Hasirci VN, Alaeddinoglu NG (1995) Biomaterials 16: 761-768
22. Arica MY, Hasirci VN (1993) Polym. International 32: 177-182
23. Asua JM, Rodriguez VS, Sudol ED, El-Aasser MS (1989) J Polym. Sci, Polym. Chem Ed 27: 3569-3587
24. Capek I, Barton J, Karpatyova A (1987) Makromol. Chem. 188: 703
25. Nomura M, Fujita K (1989) Makromol Rapid Commun 10: 581
26. Capek I, Riza M, Akashi M (1992) Polym J 24: 959
27. Chu H-H, Piirma I (1989) Polym Bull (Berlin) 21:301
28. Fitch RM, Tsai CH (1971) In: Fitch RM (ed) Polymer Colloids, Plenum Press, New York (pp 73)
29. Fitch RM (1973) Br Polym J 5: 467
30. Lichti G, Gilbert RG, Napper DH (1983) J Polym Sci, Polym Chem Ed 21: 269
31. Feeney PJ, Napper DH, Gilbert RG (1984) Macromol 17: 2520
32. Feeney PJ, Napper DH, Gilbert RG (1987) ibid 20: 2922
33. Chu H-H, Lin C-S (1999) Porceedings of 22nd Polymer Symposium, Hsin-Chu, Taiwan (pp. 261-2)
34. Fu D-C (1996) M.S. Thesis, Feng Chia University (Taichung, Taiwan)