Sonochemical Polymerization of Acrylic Acid and Acrylamide in the Presence of a New Redox System— A Comparative Study

R. Anbarasan,[1] J. Jayaseharan,[2] M. Sudha,[3] A. Gopalan[3]

[1]*Department of Leather Technology, Priyadarshini Engineering College, Vaniyambadi 635 751, Tamil Nadu, India*
[2]*Department of Biomedical Engineering, Case Western Reserve University, Cleveland, Ohio 44106*
[3]*Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamil Nadu, India*

ABSTRACT: Acrylic acid and acrylamide were polymerized by a peroxydisulfate–suberic acid redox system under a nitrogen atmosphere both in the presence and in the absence of ultrasound (at constant frequency). The rate of polymerization was determined for different concentrations of monomer, initiator, and activator and for different percentages of ultrasonic intensity. The polymers were characterized by X-ray diffraction and ^{1}H-NMR spectroscopy. A probable mechanism is proposed to explain the experimental results obtained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3685–3692, 2003

Key words: acrylic acid; acrylamide; redox system; ultrasound; XRD; ^{1}H-NMR spectroscopy; mechanism

INTRODUCTION

Ultrasounds are compressional waves in the air that have frequencies higher than 20,000 Hz. High-energy ultrasound (US) is used in many ways, such as to kill bacteria in liquid, for welding, drilling, melting, and soldering; and as an accelerator for chemical reactions.[1] It is well known that US induces mechanical, thermal, and oxidative effects on materials in the liquid because of the cavitation process.[2,3] The ultrasonic effect has also been applied to the polymerization of vinyl monomers and the degradation of polymer materials.[4] For the polymerization of vinyl monomers, US directly initiates polymerization, even in the absence of initiators.[5,6] It was found that when a polymer solution was irradiated by US, the degree of polymerization was reduced because of various ultrasonic factors such as ultrasonic intensity and frequency, the nature of the solvent, and the irradiation temperature and pressure.[7,8] A study of ultrasonic degradation on polymer solutions was carried out by Paladhi et al.[9]

Price and coworkers[10] used US to investigate the degradation behavior of poly(acrylic acid) (PAA) in various solvents. They reported that the extent of polymer degradation depends on the cavitational behavior of the solvent used. The rate of decomposition of peroxydisulfate (PDS) in the presence and in the absence of US at ambient temperature was reported by Price et al.[11] Recently, many researchers have reported the effect of US on the radical polymerization of various vinyl monomers. US was shown to be a useful tool for initiating the radical emulsion polymerization of methyl methacrylate (MMA) at low temperature.[12] In 1992 Stoffer and coworkers[13] reported the ultrasonically initiated free-radical-catalyzed polymerization of acrylamide. US-initiated free-radical copolymerization of styrene and maleic anhydride also has been reported.[14] Recently US was used as an initiator for the polymerization of methacrylamide and acrylamide[17,18] in the presence of peroxosalts as a chemical initiator. Vivekanandam et al.[19] reported about PDS-initiated cyclopolymerization of diallylamine in the presence of US, for which they determined the rate parameters. US also has been used as an initiator for graft copolymerization of methyl methacrylate onto regenerated cellulose film in the presence of ceric salt.[20]

Most of the effects of ultrasonic irradiation on polymer degradation and synthesis described above have been generally attributed to the cavitation phenomenon, both in the presence and in the absence of an initiator. The use of US in polymer synthesis alters not only the kinetic parameters but also the properties of the polymers. In the same vein, this article takes up for the first time the kinetics of US-initiated polymerization and an analysis of polymer such as crystallinity and NMR spectroscopy.

EXPERIMENTAL

Materials

Acrylic acid (AA; SRL AR, India) was used after distillation under vacuum. Acrylamide (AcA; CDH AR)

Correspondence to: R. Anbarasan (anbu_may3@yahoo. co.in).

was recrystallized from alcohol prior to polymerization. Peroxydisulfate (PDS; CDH AR, India), suberic acid (SA; CDH AR, India), and acetone (Ranbaxy AR) were used without further purification.

Procedure

Definite volumes of aqueous solutions of monomer (AA or AcA) and activator (SA) were placed in a specially designed polymerization vessel that contained one water inlet and one outlet and were deaerated for 15 min by passing pure nitrogen gas through the nozzle. Polymerization was initiated by the addition of a calculated volume of PDS with simultaneous ultrasonic irradiation at a constant frequency of 40 MHz with 50% intensity. The overheating and increase in pressure during ultrasonic irradiation were reduced by carrying out the reaction at a normal ultrasonic intensity value (50%). Because of the exothermic nature of the cavitation process of ultrasonic irradiation, US liberates heat energy; so the reaction temperature was maintained at 32°C by circulating ice-cold water during the ultrasonic irradiation. The polymer thus formed (PAA) was filtered through a previously weighed (W_1) G4 sintered crucible. The crucible was dried to a constant weight (W_2) and weighed. The difference between W_1 and W_2 was the weight of the polymer formed. For AcA the polymer solution was treated with acetone to precipitate the polymer and then filtered. The rate of polymerization was estimated using the gravimetric method.

$$R_p = \frac{(W_2 - W_1)}{V.t.M.} \times 1000$$

where $W_2 - W_1$ is the weight of the polymer formed, V is the total reactant volume, t is the reaction time, and M is the molecular weight of the monomer used.

Ultrasonic vibrator

US was produced from the ultrasonic vibrator probe of the surface area, 22.5×10^{-2} cm^2, at a frequency of 50 MHz. All the experiments except the one for ultrasonic intensity variation were carried out at 50% ultrasonic intensity. The top right corner of the instrument contained an semicircular-shaped intensity variation part that showing the intensity from 0 to 100. The intensity could be adjusted by turning the knob to move the arrow marker. Generally the knob was fixed at a 50% intensity. By adjusting the knob, the required amount of intensity could be obtained at the same frequency. Before and after the polymerization process, the ultrasonic probe was washed by passing the US in water for 10 min.

X-ray diffraction analysis

X-ray diffraction (XRD) was recorded for the samples prepared in the presence and in the absence of US by using a STOESTADI/P instrument in the transmission mode ($2\theta = 5°–40°$) using a precalibrated detector. The XRD patterns were taken with monochromatized Cu kα1, ($\lambda = 1.54056$ A^0) radiation.

^{1}H-(Decoupled) NMR spectroscopy

The proton NMR spectroscopy was recorded for both PAA and PAcA synthesized in the presence and in the absence of US by using a Bruker Ac-F 200 FT-NMR spectrometer instrument in CDCl$_3$.

Molecular weight

The molecular weights of PAA and PAcA were determined from viscosity measurement of the polymer in aqueous solutions of 1,4-dioxane (1.0M) and sodium nitrate (1.0M), respectively, at 32°C by using the following equations:

$$[\eta] = 76.0 \times 10^{-3} \, [\overline{\mathrm{Mw}}]^{0.50} \text{ and}$$

$$[\eta] = 3.73 \times 10^{-4} \, [\overline{\mathrm{Mw}}]^{0.66}$$

RESULTS AND DISCUSSION

Effect of [AA] or [AcA] on R_p

AA was varied between 0.275 and 0.608 mol/L while keeping other experimental conditions constant. It was observed that the R_p increased with an increase in [AA]. To find out the order dependence, plots were done of log [AA] versus log R_p [in the presence of US Fig. 1(a)] and log [AA] versus log R_p in the absence of US [Fig. 1(b)]. The plots showed the first-order dependence of [AA] on R_p both in the presence and in the absence of US. The first-order dependence of [AA] on R_p was further confirmed from the plots of [AA] versus R_p in the presence of US [Fig. 1(c)] and [AA] versus R_p in the absence of US [Fig. 1(d)]. The plots were found to be linear and to pass through the origin.

AcA concentration was varied between 0.275 and 0.608 mol/L while keeping other experimental conditions as constant. It was found that R_p increased with increase in [AcA] both in the presence and in the absence of US. But in the presence of US the R_p was found to be higher than in its absence. This may have occurred for the following reasons: (1) the auto acceleration effect and cavitation process as a result of US; (2) thermal activation from the collapse of microbubbles[12]; (3) production of OH radicals from water solvent by US irradiation; (4) in an aqueous medium the US very quickly decomposing the PDS and SA to
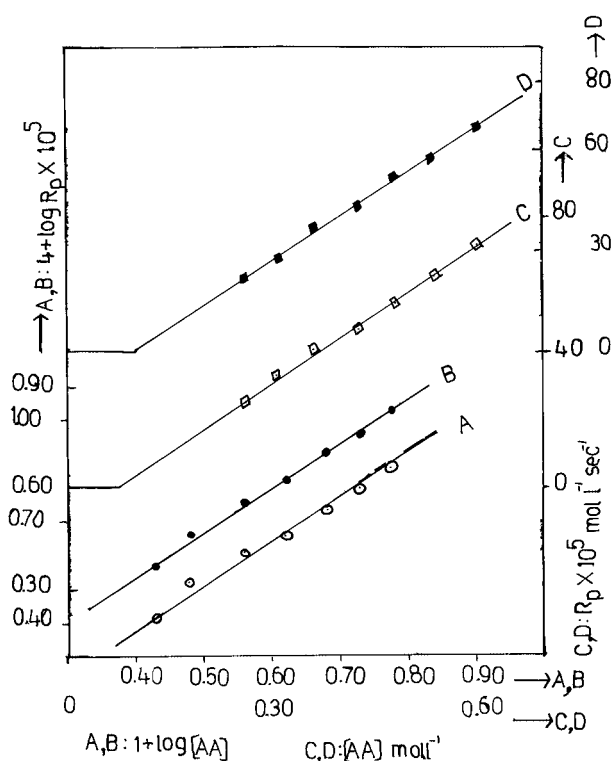
Figure 1 Effect of [AA] on R_p ([PDS] = 10.0×10^{-4} mol/L, [SA] = 5.12×10^{-4} mol/L, temperature = 32°C, time = 900 s, US frequency = 50 MHz, US intensity = 50%).

Effect of [PDS] on R_p

The effect of PDS on R_p for the AA system was studied by varying the concentration of PDS between 2.50×10^{-4} and 17.5×10^{-4} mol/L while keeping other experimental conditions constant. Very interesting to note was that the R_p increased with an increase in PDS both in the presence and in the absence of US. This may be a result of the formation of a large number of free radicals from PDS, which is responsible for the initiation of the polymerization process.[13]

But the R_p was found to be higher in the presence of US (even in lower concentrations of PDS) than in its absence. The reason for the increase in R_p in the presence of US was explained earlier in the discussion on monomer variation. Another important factor for the increased was that US reduced the formation of side products from the radicals of PDS through simultaneous formation of OH radicals from water solvent, making possible direct interaction between the initiator radicals and monomer units.

To find out the order dependence, plots were drawn of log [PDS] versus log R_p in the presence of US [Fig. 3(a)] and log [PDS] versus log R_p in the absence of US [Fig. 3(b)]. The linear plots gave a slope value of 1, indicating the first-order dependence of [PDS] on R_p both in the presence and in the absence of US. This can be further confirmed by plotting [PDS] versus R_p in the presence of US [Fig. 3(c)] and [PDS] versus R_p in

SO_4^{2-} and SA^{2-}; (5) US producing a vigorous stirring effect, leading to a possible combination of the monomer radicals; and (6) during the process US generating high pressure that enhanced the forward (polymer formation) reaction rather than the backward reaction (dissociated to monomer radicals).

AA had a higher R_p value than AcA, both in the presence and in the absence of US. The lesser activity of AcA can be ascribed to the steric repulsion caused by the bulky amide group present on the double-bond-containing carbon atom. When [AA] or [AcA] was increased, the R_p was also found to increase, even in the absence of US. Possible explanations for this are: (1) an increasing number of monomer radicals; (2) an increase in viscosity of the medium, that is, the gel effect resulting from the solubility of some dimers and trimers in the reaction medium; and (3) autoacceleration or surface effect because of the formed PAA or PAcA.
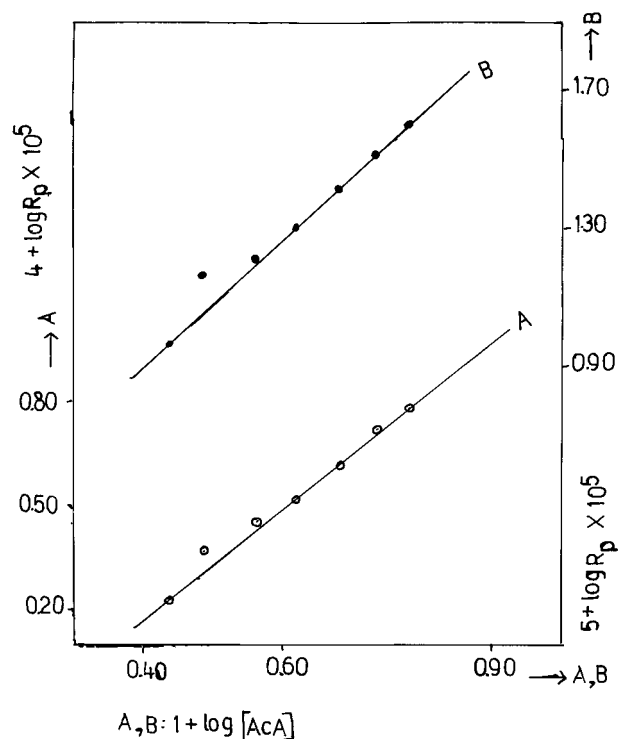
To find out the order dependence, the following plots were made: log [AcA] versus log R_p in the presence of US [Fig. 2(a)] and log [AcA] versus log R_p in the absence of US [Fig. 2(b)]. The slope of these plots indicated the 1.5 and 2.0 order dependence of AcA on R_p (both in the presence and in the absence of US). In the absence of US, higher-order dependence was noticed.

Figure 2 Effect of [AcA] on R_p ([PDS] = 10.0×10^{-4} mol/L, [SA] = 5.12×10^{-4} mol/L, temperature = 32°C, time = 900 s, US frequency = 50 MHz, US intensity = 50%).
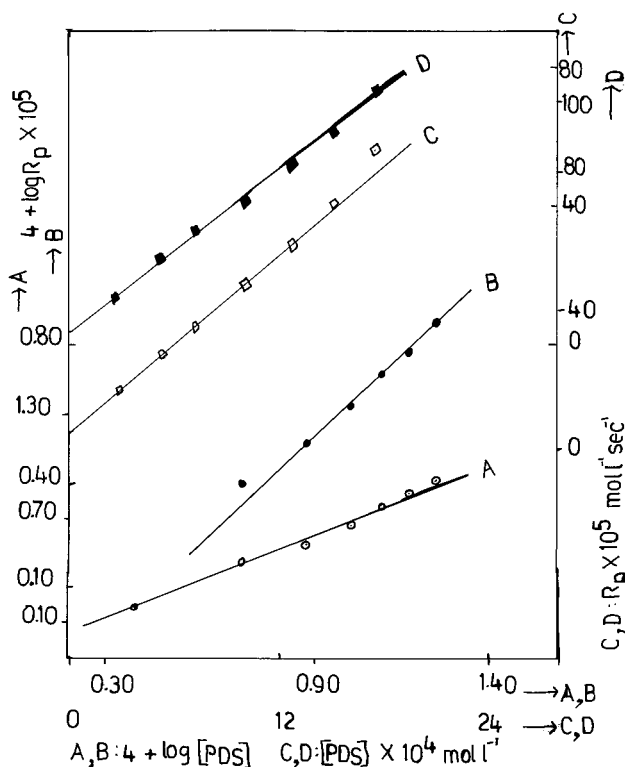
the absence of US [Fig. 3(d)]. The plots were found to be linear with a definite intercept value.

Similar plots were made for the AcA system. Here we also observed that the R_p increased with an increase in [PDS] both in the presence and in the absence of US. In the presence of US a higher R_p value was noted. [PDS] showed first-order dependence on R_p both in the presence and in the absence of US. The plots of log [PDS] versus log R_p in the presence of US, log [PDS] versus log R_p in the absence of US [Fig. 4(b)], [PDS] versus R_p [Fig. 4(c)], and [PDS] versus R_p [Fig. 4(d)] were made, and the plots were found to be linear.
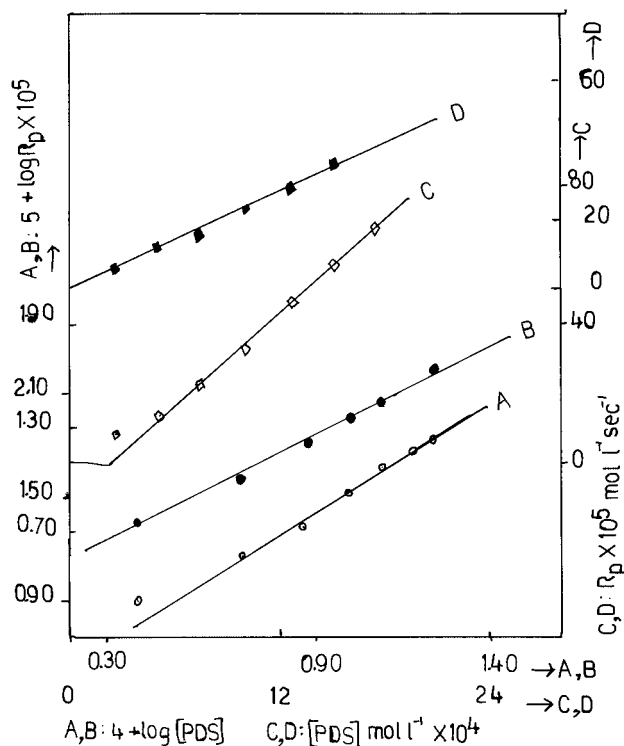
The AA system showed a higher R_p value than did the AcA system both in the presence and in the absence of US. This may be because of the rapid nature of the polymerization of AA.

Effect of [SA] on R_p

SA concentration was varied in a range from 1.25 $\times$ 10^{-4} to 8.75 $\times$ 10^{-4} mol/L while keeping other experimental conditions constant for the AA system. R_p was increased with an increase in [SA] both in the presence and in the absence of US. This can be attributed to the formation of a large number of radicals of SA. But in the presence of US the R_p was found to be slightly higher than in its absence. The reasons for this

Figure 4 Effect of [PDS] on R_p ([AcA] = 0.42 mol/L, [SA] = 5.12 $\times$ 10^{-4} mol/L, % ultrasonic intensity = 50%, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).

may be: (1) the US-accelerated formation of radicals of SA, and (2) the formation of diradicals from both carboxyl groups of SA.

The order dependence of SA was also determined. Plots were made of log [SA] versus log R_p in the presence of US [Fig. 5(a)] and log [SA] versus log R_p in the absence of US [Fig. 5(b)]. The slope of the plots indicated 0.5 order dependence of [SA] on R_p both in the presence and in the absence of US. As usual, in the presence of US the R_p was found to be higher than in its absence. This may be a result of the rapid formation of radicals of SA. The 0.5 order dependence was further confirmed by plotting $[SA]^{1/2}$ versus R_p in the presence of US [Fig. 5(c)] and $[SA]^{1/2}$ versus R_p in the absence of US [Fig. 5(d)], and the plots were found to be linear with definite intercept values.

Similar plots were made for the AcA system (Fig. 6). Here, also, we found the same order (0.5) dependence on R_p. The R_p of the AA system was somewhat higher that that of the AcA system, both in the presence and in the absence of US. The lower value of R_p for both in the presence and in the absence of US indicated that AcA was the dullest monomer.

Figure 3 Effect of [PDS] on R_p ([AA] = 0.42 mol/L, [SA] = 5.12 $\times$ 10^{-4} mol/L, % ultrasonic intensity = 50%, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).

Effect of percentage of ultrasonic intensity on R_p

The effect of percentage of ultrasonic intensity on R_p for the AA system was studied by varying the inten-
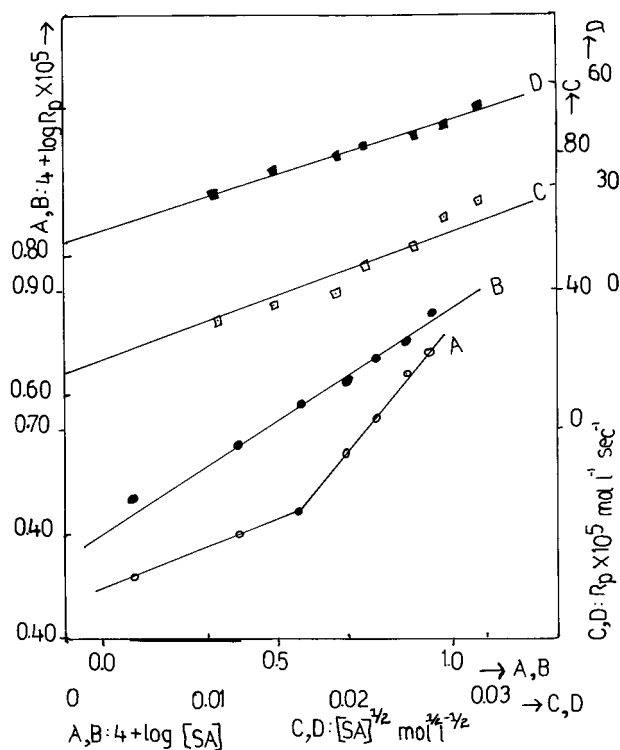
Figure 5 Effect of [SA] on R_p ([AA] = 0.42 mol/L , [PDS] = 10.0 × 10^{-4} mol/L, % ultrasonic intensity = 50%, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).
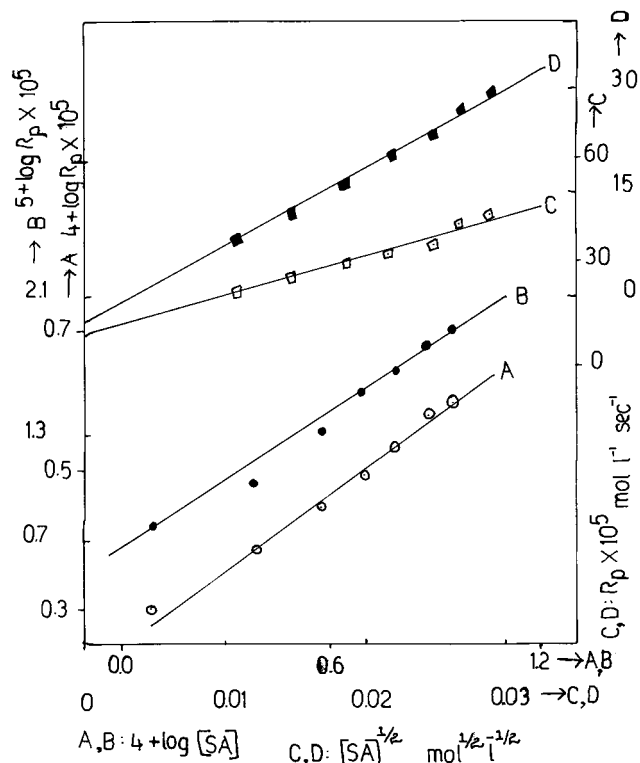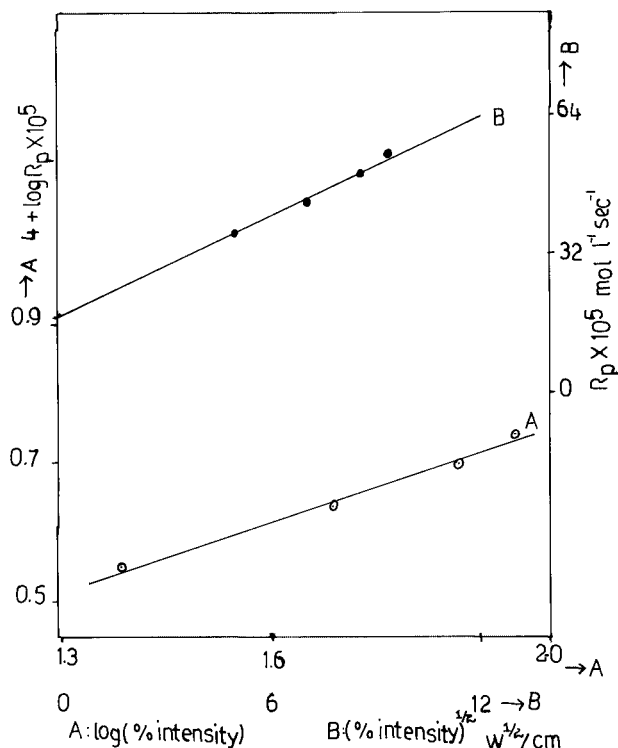

Figure 6 Effect of [SA] on R_p ([AcA] = 0.42 mol/L, [PDS] = 10.0 × 10^{-4} mol/L, % ultrasonic intensity = 50%, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).

sity from 25% to 90% while keeping other experimental conditions constant. It was very interesting to note that the R_p was increased while increasing the ultrasonic intensity. This may be for the following reasons: (1) while ultrasonic intensity was increased, the temperature and pressure produced also were increased; (2) the cavitational process was increased[14]; (3) the stirring effect gradually was increased; and (4) the activation of radical formation was increased through the decomposition of PDS, SA, and water solvent.

To find out the order dependence for the AA system, the plot of log(% intensity) versus log R_p [Fig. 7(a)] was made. The plot was found to be linear and the slope value indicated 0.5 order dependence. The half-order dependence on R_p was further confirmed by plotting (% intensity)$^{1/2}$ versus R_p [Fig. 7(b)].

Similar plots also were made for the AcA system (Fig. 8). The plot of log(% intensity) versus log R_p [Fig. 8(a)] was made, and the slope value was found to be 1. The first-order dependence was further confirmed by plotting (% intensity) versus R_p [Fig. 8(b)], which was found to be linear.

Now the AA and AcA systems will be critically compared. At a lower percentage of ultrasonic intensity the AcA showed a high R_p value. The percentage of ultrasonic intensity variation of the AA system showed half-order dependence on R_p, whereas the

Figure 7 Effect of percent ultrasonic intensity on R_p ([AA] = 0.42 mol/L, [PDS] = 10.0 × 10^{-4} mol/L, [SA] = 5.12 × 10^{-4} mol/L, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).
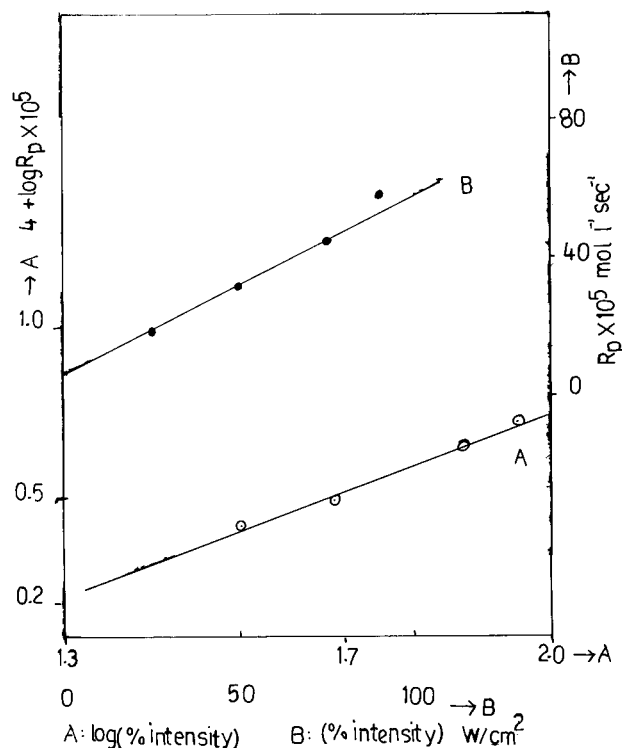
Figure 8 Effect of percentage of ultrasonic intensity on R_p (AcA = 0.42 mol/L, PDS = 10.0 × 10^{-4} mol/L, SA = 5.12 × 10^{-4} mol/L, ultrasonic frequency = 50 MHz, temperature = 32°C, time = 900 s).

AcA system showed first-order dependence. This indicates that AcA was a duller monomer than AA and became active only in the presence of US as a cocatalyst. The dullest activity of AcA was a result of the presence of a bulky amide group on the double-bond-containing carbon atom.

Molecular weight

It was found that the viscosity average molecular weight was lower in the presence of US that in its absence for both the AA and AcA systems. This may be a result of the ultrasonic degradation of the polymer chains formed. Ultrasonic degradation was found to be much higher for the AA system than for the AcA system (Tables I and II). This can be ascribed to the fast chain-growing nature of the AA system, in which chain growth and chain degradation were competitive. For AcA, this produced a disproportionate number of polymer radicals that activated the chain growth. Now US acted as a cocatalyst and increased the molecular weight with slight ultrasonic degradation.

The viscosity average molecular weight was determined for polymers obtained with different ultrasonic intensities. The results indicated that molecular weight increased with an increase in the percentage of ultrasonic intensity to a maximum limit (50%), beyond

TABLE I
Molecular Weight

| System | Viscosity average molecular weight | |
	Presence of US	Absence of US
AA–PDS–SA	112,500	131,000
AcA–PDS–SA	65,400	70,100

which it reduced the molecular weight for both the AA and AcA systems. Because of severe degradation at higher percentages of ultrasonic intensity (90%), molecular weight was reduced.

XRD analysis

PAA and PAcA synthesized both in the presence and absence of US were subjected to XRD analysis (figure not included). Improvement in crystallinity in the presence of US was not observed because of the absence of crystalline peaks.

^{1}H-NMR (decoupled) spectroscopy

The above-mentioned synthesized polymers were subjected to ^{1}H-decoupled-NMR spectroscopy (figure not included). It showed a triplet peak (polymer synthesized in the presence of US) and singlet peak (polymer synthesized in the absence of US). Further investigations are ongoing.

Mechanism

Polymer sonochemistry has been an active field since Demann et al.[21–23] used US for polymerization in 1930. It is generally accepted that the cause of ultrasonic depolymerization is cavitation or shock waves generated during ultrasonic irradiation.[22] When a long-chain polymer is sonicated, it is known that it preferentially breaks at the middle, and long-chain radicals result.[24,25] The formation of long-chain radicals was confirmed by Tabata and coworkers[26,27] during ultrasonic irradiation of poly(methyl methacrylate), polystyrene, and poly(vinyl alcohol) through ESR techniques. Husceste et al.[28] reported that during ultrasonic irradiation two types of termination processes took place: disproportionation and combination.
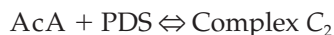
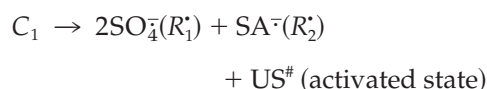**TABLE II**
Molecular Weight at Different Percentages
of US Intensity

System	Ultrasonic intensity (%)	Molecular weight
AA–PDS–SA	25	105,000
	90	824,000
AcA–PDS–SA	25	40,800
	90	62,000

Hunkeler and colleagues[29] reported that any nitrogen-containing monomer can form a complex with the initiator PDS.

Based on the above available literature, a probable mechanism has been proposed with some modifications.[1] Here we used 50% ultrasonic intensity for polymer synthesis, which led to mild ultrasonic degradation. This was shown by the molecular weight of the polymer formed. But at higher ultrasonic intensity the degradation was found to be higher with an increase in R_p. These two facts help to show that at lower ultrasonic intensity the recombination process is encouraged, whereas at higher ultrasonic intensity the disproportionation process is favored. The mechanism is as follows:
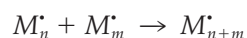
Initiation

$$PDS + SA + US \Leftrightarrow Complex\ C_1$$

$$C_1 \rightarrow 2SO_4^-(R_1^\bullet) + SA^-(R_2^\bullet)$$

$$+ US^\# \text{ (activated state)}$$

$$US^\# + H_2O \rightarrow {}^\bullet OH(R_3^\bullet)$$

$$AcA + PDS \Leftrightarrow Complex\ C_2$$

$$C_2 \rightarrow 2SO_4^-(R_1^\bullet) + M$$

$$AA + SO_4^- \rightarrow AA^\bullet + Products$$

$$[AA, AcA = M]$$

Propagation

$$SO_4^- + M \rightarrow M_1^\bullet + Products$$

$$SA^-{}_4 + M \rightarrow M_1^\bullet + Products$$

$${}^\bullet OH + M \rightarrow M_1^\bullet + Products$$

$$M_1^\bullet + M \rightarrow M_2^\bullet$$

$$M_2^\bullet + M \rightarrow M_3^\bullet$$

$$- - - - - - - - - - - - - - - - - - - -$$
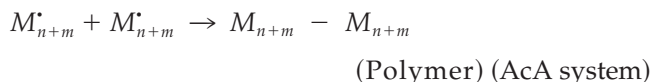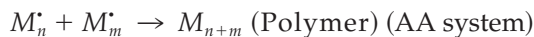
$$M_n^\bullet + M_m^\bullet \rightarrow M_{n+m}^\bullet$$

Termination

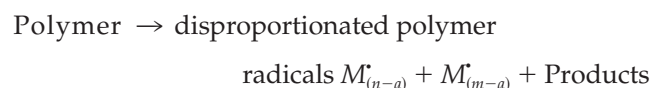AA system leads to unimolecular termination whereas AcA system leads to biomolecular termination

$$M_n^\bullet + M_m^\bullet \rightarrow M_{n+m} \text{ (Polymer) (AA system)}$$

$$M_{n+m}^\bullet + M_{n+m}^\bullet \rightarrow M_{n+m} - M_{n+m}$$

$$\text{(Polymer) (AcA system)}$$

At lower ultrasonic intensity

$$M_n^\bullet + M_m^\bullet \Leftrightarrow M_{n+m} \text{ (Polymer)}$$

$$M_{n+m} \rightarrow M_{(n+m)-a}$$
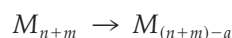
Where $a = 1, 2, 3 \ldots$ (number of segments)

At higher ultrasonic intensity

$$M_n^\bullet + M_m^\bullet \rightarrow M_{n+m} \text{ (Polymer)}$$

$$Polymer \rightarrow \text{disproportionated polymer}$$

$$\text{radicals } M_{(n-a)}^\bullet + M_{(m-a)}^\bullet + Products$$

When the percentage of ultrasonic intensity was increased, the value of a also increased for both the AA and AcA systems. The above mechanism explains the experimental results obtained.

CONCLUSIONS

From the above kinetic study the following observations were made: (1) the R_p was found to be higher for the AA system than for the AcA system both in the presence and in the absence of US; (2) the R_p was higher in the presence of US than in its absence for both system; (3) ultrasonic vibration took place, with the simultaneous emission of heat energy; (4) cavitation accounted for the increase in R_p (in the presence of US) for both systems; (5) in the presence of US the molecular weight was reduced; (6) crystallinity was not improved, even in the presence of US; (7) in the presence of US the ^{1}H-NMR (decoupled) spectra showed a triplet peak, whereas in the absence of US it showed a singlet peak in the same regions; and (8) US was used as a cocatalyst for both systems, particularly for the AcA system.

References

1. Stucher, J. E.; Bernaswni, C. F. Ultrasonic Methods in Investigations of Rates and Mechanism of Reactions; Wiley: New York, 1986.
2. Nothingk, B. E.; Neppiras, E. A. Proc Phys Soc 1950, 63, 674.
3. Richards, W. T.; Loomis, A. L. Am Chem Soc 1927, 49, 3086.

4. Kruus, P. Ultrasonics 1983, 21, 201.
5. Kruus, P.; Patraboy, J. J. J Phys Chem 1985, 89, 3379.
6. Peters, D. J Mater Chem 1996, 6, 1605.
7. Weissler, A. J Appl Phys 1950, 21,171.
8. Mostafa, M. A. K. J Polym Sci 1958, 33, 311.
9. Paladhi, R.; Singh, R. P. Eur Polym J 1994, 30, 251.
10. Price, G. J.; Smith, P. F. Eur Polym J 1993, 29, 419.
11. Price, G. J.; Glifton, A. A. Polymer Commun 1996, 37, 3971.
12. Joechou, H. C.; Stoffer, J. O. J Appl Polym Sci 1999, 72, 827.
13. Joechou, H. C.; Stoffer, J. O. J Appl Polym Sci 1999, 72, 797.
14. Stoffer, J. O.; Sitton, O. C.; Kim, Y. Polym Mater Sci Eng 1992, 67, 242.
15. Vivekanandam, T. S.; Umapathy, S.; Gopalan, A. J Polym Mater 1998, 15, 261.
16. Vivekanandam, T. S.; Umapathy, S.; Gopalan, A. J Appl Polym Sci 2000, 76, 524.
17. Vivekanandam, T. S.; Umapathy, S.; Gopalan, A. Polymer Commun 1999, 40, 807.
18. Vivekanandam, T. S.; Umapathy, S.; Gopalan, A. J Polym Sci Chem Ed 1998, 36, 2715.
19. Vivekanandam, T. S.; Umapathy, S.; Gopalan, A. Eur Polym J 2000, 36, 385.
20. Kondo, T.; Kubota, A.; Katakai, R. J Appl Polym Sci 1999, 71, 251.
21. Suslick, K. S. Ultrasound, Its Chemical, Physical and Biological Effects; VCH Publishers: New York, 1988.
22. Mason, T. J.; Lorimer, J. P. Theory, Applications and Uses of Ultrasound in Chemistry; Ellis Harwood Limited, John Wiley: New York, 1988.
23. Ley, S. V.; Low, C. M. R. Ultrasound in Synthesis; Springer Verlag: London, 1980.
24. Mason, T. J. Chem Soc Reviews 1997, 26, 443.
25. Price, G. J. Chem Ind 1993, 1, 75.
26. Tabata, M.; Miyazawa, T.; Sohma, J. Chem Phys Let 1980, 73, 178.
27. Tabata, M.; Sohma, J. Eur Polym J 1980, 16, 589.
28. Huceste, C.; Giz, A. Polym Bull 1999, 43, 215.
29. Hunkeler, D. Macromolecules 1991, 24, 2160.