Sonochemical Cyclopolymerization of Diallylamine in the Presence of Peroxomonosulfate

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ABSTRACT: The cyclopolymerization of a symmetrical nonconjugated diolefin, diallylamine (DA), initiated by peroxomonosulfate (PMS), proceeded only in the presence of ultrasound. The rate of polymerization showed a first-order dependence on DA and a half-order dependence on PMS concentration. The results are adequately explained through a proposed mechanism involving alternate intramolecular and intermolecular propagation reactions. The rate parameters for the cyclopolymerization are evaluated. The role of ultrasound in the initiation of cyclopolymerization is discussed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1548–1553, 2005

Key words: cyclopolymerization; kinetics (polym); radical polymerization; initiators

INTRODUCTION

Monovinyl polymerization studies of acrylamide (AA) with peroxodisulfate (PDS)[1] and peroxomonosulfate (PMS) as initiators[2] have been done earlier. To determine the reactivity difference, a CH_3 substituted in the alpha-position monomer, methacrylamide (MMA), with PDS as an initiator has also been studied.[3] Similarly, the divinyl polymerization initiated by PDS has been reported by our research group[4] and also as one component of a redox pair.[5–8] Free-radical-initiated polymerization reactions have been carried out for the divinyl monomers, in particular for diallyl dialkyl ammonium halides.[9] The thermal decomposition[10] of PDS has been found to be catalyzed by an ultrasonic field.[11] Taking advantage of the ultrasonic decomposition of PDS, we studied the polymerization of monovinyl monomers, such as AA and PDS,[12] AA and PMS,[13] MMA and PDS,[14] and MMA and PMS,[15] in the presence of ultrasonic waves. After this, we also carried out the polymerization of a divinyl monomer, diallylamine (DA), and PDS in the presence of ultrasound in our laboratory.[16] In our earlier work,[16] we observed that the use of the divinyl monomer, the symmetrical nonconjugated diolefin DA, resulted in a gel-free polymerization with smooth kinetics when DA was polymerized in the presence of ultrasound and PDS. Chain propagation involving cyclopolymerization was invoked to explain the results with the suggestions put forth by Butler and Ingley.[17] We have now obtained evidence for this type of propagation with the same monomer with PMS in the presence of ultrasound, and the results are reported here.

EXPERIMENTAL

Potassium PMS (oxone) was a gift sample from Du-Pont Co. and was used as received. DA (E. Merck, Darmstadt, Germany) was used without further purification. The monomer was assayed for double-bond concentration through bromometry. All other reagents were analar grade and were used as received. Deionized water was distilled over alkaline permanganate in an all-glass apparatus and was used to prepare the solutions.

The monomer DA and the PMS solutions were prepared fresh daily and were estimated by bromometry and iodometry, respectively.

An ultrasonic interferometer and a thermostatable double-walled cell supplied by M/s Mittal Enterprises (Delhi, India) were used for the aqueous polymerization of DA. A solution of a requisite amount of DA taken in the reaction cell and a constant-temperature bath (M/s Toshniwal Brothers, Chennai, India) were used to circulate water through the outer jacket of the reaction cell to maintain the required temperature at an accuracy of ±0.1°C. The PMS solution, equilibrated at the experimental temperature, was added to the reaction mixture in the cell, and a constant ultrasonic frequency of 1 MHz (with an intensity of 0.7 mW/

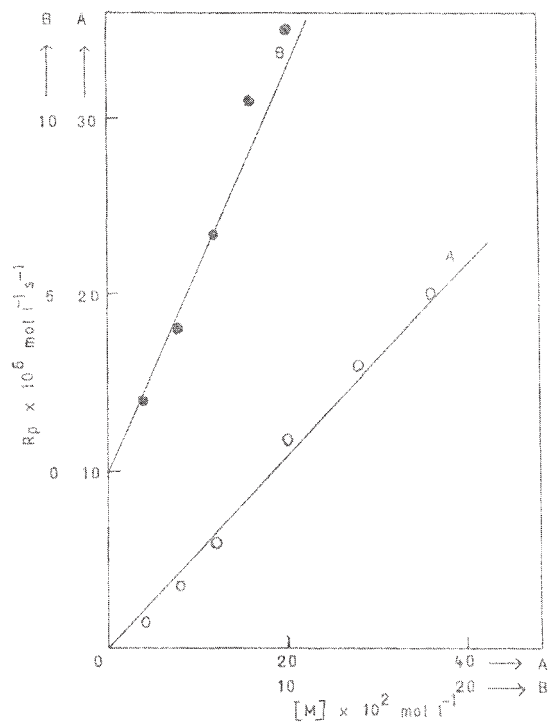*Correspondence to:* T. S. Vivekanandam (mkuvivek@rediffmail.com or s_umapathy@hotmail.com).

Figure 1 Dependence of R_p on [M] in the presence of ultrasound (temperature = 35°C, frequency = 1 MHz): [PMS] = (A) 10.8×10^{-4} and (B) 21.6×10^{-4} mol/L.

cm²) was applied with the interferometer to this reaction mixture. The time of passing ultrasound was taken as the starting time of polymerization. The rate of polymerization ($R_p = -d$[Double bond]$/dt$) was determined by the monitoring of the concentration of the unreacted monomer after polymerization by bromometry.

RESULTS AND DISCUSSION

In general, cyclopolymerization reactions are dependent on the reactivity of the monomer and its concentration range, the solvent used, the temperature of the system, and the type of the initiator employed. The product, a cyclic polymer, may be either soluble or insoluble in water; this depends on the nature of the intermediate steps involved during polymerization to yield a five- or six-membered polymer under kinetic and/or thermodynamic control. The ring size in cyclopolymers are influenced by the relative abilities of the intermediate radicals and the orientation of the double bonds present at the end of a divinyl monomer. However, cyclopolymerization could lead to the thermodynamically favored ring via the more stable radical, to the ring via the less stable radical, or to a mixture of both.

In this study, the polymerization of DA did not occur without PMS in the presence of ultrasound. However, polymerization did occur in the presence of

ultrasound and PMS. This indicated that the monomer DA could not be polymerized in the presence of ultrasound alone. Hence, polymerization studies were carried out only in the presence of PMS and ultrasound.

R_p was followed for the polymerization of DA in the concentration range $4–36 \times 10^{-2}$ mol/L with PMS ($5–32 \times 10^{-4}$ mol/L) in the presence of ultrasound.

R_p was followed for various monomer concentrations ([M]'s) with the PMS concentration ([PMS]) and ultrasound frequency (1 MHz, intensity = 0.7 mW/cm²) kept constant. From the plot of R_p versus log [M], the order with respect to the monomer was found to be unity. This was verified with a plot of R_p versus [M] (Fig. 1). This was a straight line passing through the origin and suggested a first-order dependence of R_p on [M]. We further confirmed this dependence by following R_p with a different set of [PMS]'s and an ultrasound frequency of 1 MHz.

R_p was also followed for various [PMS]'s with [M] and the frequency of ultrasound kept constant. R_p increased with increasing [PMS], and a log R_p versus log [PMS] plot was drawn to determine the dependence of R_p on [PMS]. From this plot, the dependence was found to be half, and a plot of R_p versus [PMS]$^{1/2}$ (Fig. 2) was also drawn to verify this. The straight-line nature of the plot pointed out the half-order dependence of R_p on [PMS], and this dependence was fur-
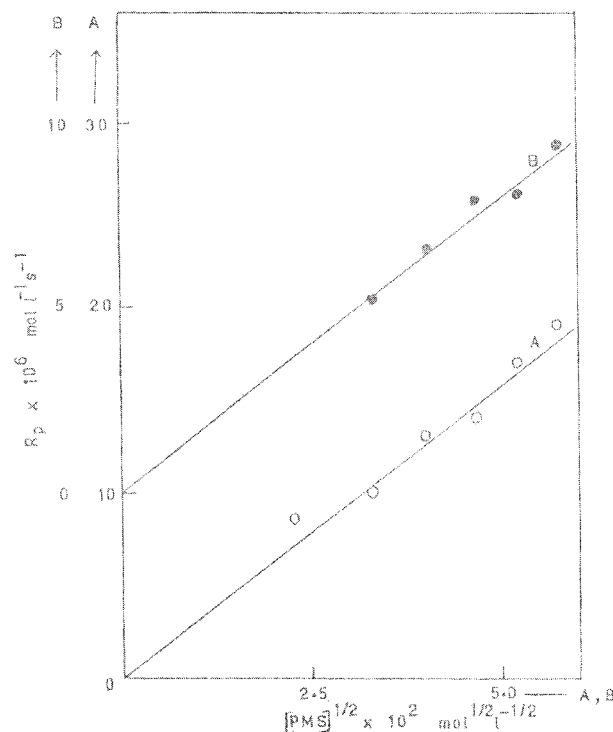

Figure 2 Dependence of R_p on [PMS]$^{1/2}$ in the presence of ultrasound (temperature = 35°C, frequency = 1 MHz): [M] = (A) 20.0×10^{-2} and (B) 11.8×10^{-2} mol/L.

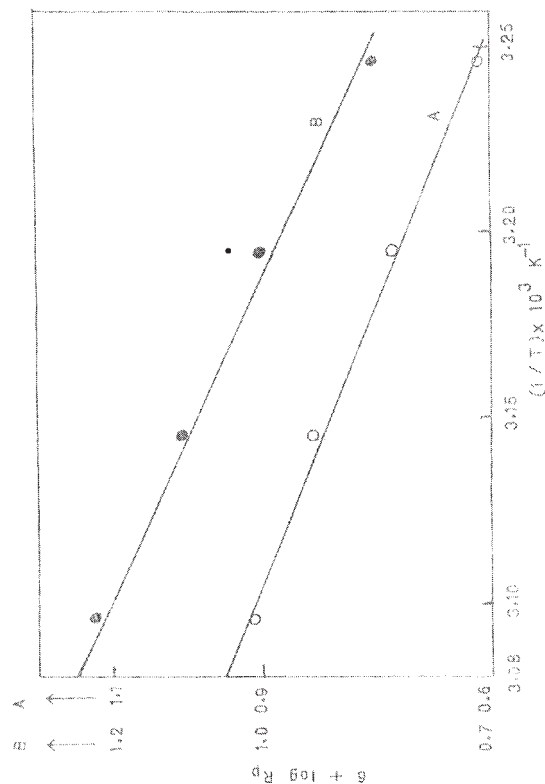**Figure 3** Dependence of R_p on temperature in the presence of ultrasound (frequency = 1 MHz, [PMS] = 10.8×10^{-4} mol/L): [M] = (A) 7.92×10^{-2} and (B) 11.8×10^{-2} mol/L.

ther justified from a different set of experiments (Fig. 2).

R_p was followed for different temperatures (35–50°C) with two different set of experimental conditions. The slope of the Arrhenius plot, log R_p versus $1/T$ (Fig. 3), gave the overall activation energy (E_a) for the polymerization of DA in the presence of ultrasound and PMS as 44 kJ/mol. From the slope and intercept of the Eyring plot, log (R_p/T) versus $1/T$, the enthalpy and entropy of activation were obtained as 44 and −31 J/deg/mol, respectively.

The observed kinetics in this study were similar to those observed for the polymerization of DA with PDS in the presence of ultrasound;[16] this suggests that the mechanistic schemes may be similar. The results of the polymerization dynamics of symmetrical nonconjugated diolefin seem to indicate that whereas the initiation and termination processes are similar to those in monovinyl polymerization,[13] it involves a different mechanism for propagation.[18] Therefore, we propose a reaction scheme incorporating cyclopolymerization as the propagation step to derive the rate expression (Scheme 1).

In Scheme 1, M_1 is either of the double bonds of previously unreacted symmetrical monomer, and $M_1 \cdot$ cyclizes. M_3 may be taken as the pendant double bond present in $M_1 \cdot$ capable of being a new site of a radical
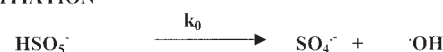
attack. $M_3 \cdot$ is the radical generated from such an attack of a radical on this pendant double bond (Scheme 2).

For the propagation, there can be two competing reactions: (1) the intramolecular cyclization of $M_1 \cdot$ between the radical part and the double bond present in the same repeating unit, which forms a new cyclized radical as in step II(a) in Scheme 1, and (2) the normal intermolecular propagation, as shown in step II(b) in Scheme 1, which forms a radical containing the unreacted pendant double bond. The relative probabilities for the existence of these two modes will depend on certain factors. The ease of the intermolecular cyclization depends on the structure of the monomer.
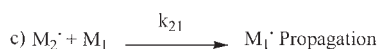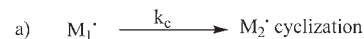
In divinyl polymerization, the presence of pendant groups hinder the monovinyl-type intermolecular propagation by step II(b). With increasing length of the pendant group, its bulkiness increases and provides more shielding for the radical to approach. With such a lowered interaction, the probability for linear propagation decreases. Hence, M_3 formation is also low. Furthermore, the concentration of monomer DA used in this study was low, and therefore, $M_1 \cdot$ would have had relatively little opportunity for linear propagation with other monomer molecules versus intramolecular cyclization. Hence, reaction step II(b) and the crosslinking between $M_1 \cdot$ and M_3 were assumed to be negligible or less probable.

There is another intermolecular propagation, step II(c) in Scheme 1, in which the cyclized radical $M_2 \cdot$ reacts with $M_1 \cdot$. This can take place at a greater rate because there is no steric hindrance in a cyclized rad-
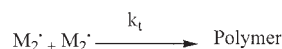
I. INITIATION

$$HSO_5^- \xrightarrow{k_0} SO_4^{\cdot -} + \cdot OH$$

$$SO_4^{\cdot -} + H_2O \longrightarrow HSO_4^- + \cdot OH$$

$$M_1 + \cdot OH \xrightarrow{k_1} M_1^{\cdot}$$

II. PROPAGATION

a) $\quad M_1^{\cdot} \xrightarrow{k_c} M_2^{\cdot}$ cyclization

b) $M_1^{\cdot} + M_1 \xrightarrow{k_{11}} M_1^{\cdot}$ linear propagation

c) $M_2^{\cdot} + M_1 \xrightarrow{k_{21}} M_1^{\cdot}$ Propagation

III. TERMINATION

$$M_2^{\cdot} + M_2^{\cdot} \xrightarrow{k_t} Polymer$$
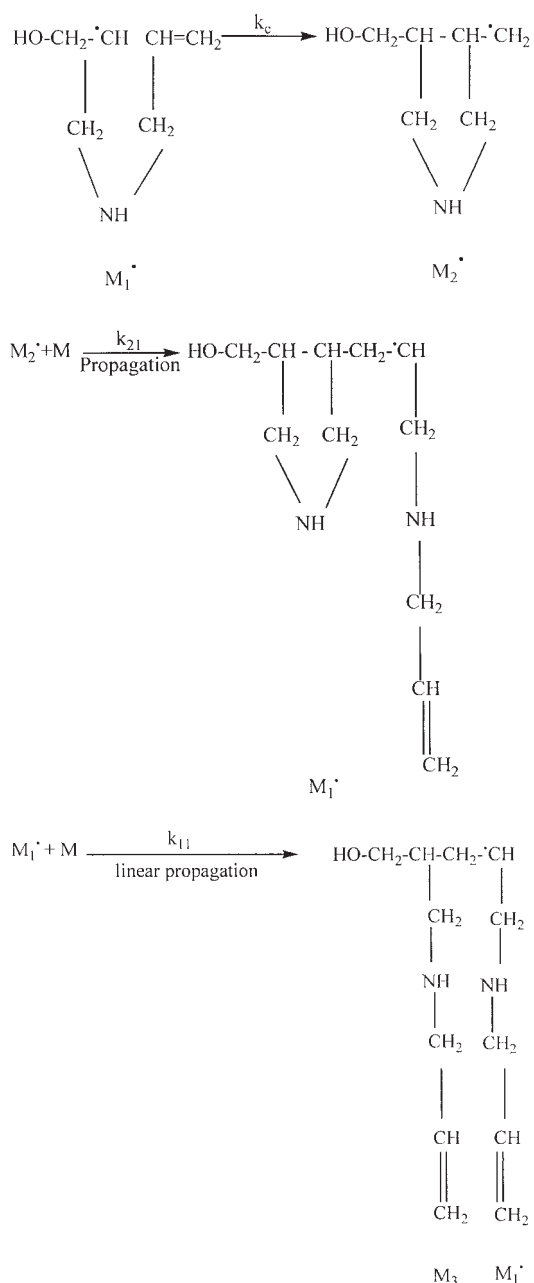
Scheme 1 k_{11} is the propagation rate constant involving M_1 and M and k_{21} is the propagation rate constant involving M_2 and M_1.

Scheme 2

tramolecular cyclization, and the second step is the intermolecular propagation through a cyclized radical, which reacts with monomer, and the sequence repeats itself. This scheme is similar to the one suggested by Buttler[20] for the polymerization of a symmetrical nonconjugated diolefin (DA here), where k_c is the cyclization rate constant and k_{21} is the intermolecular propagation reaction rate constant. For a symmetrical nonconjugated diolefin, when cyclization is the preferred path, termination is predominantly by mutual termination between growing radicals:[19,20]

$$M_1^{\cdot} \overset{k_c}{\longrightarrow} M_2^{\cdot}$$

$$M_2^{\cdot} + M_1 \overset{k_{21}}{\longrightarrow} M_1^{\cdot}$$
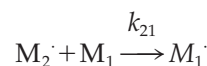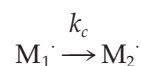
It is easy to believe that DA also would be expected to cyclize and give five-membered cyclized units because the medium was polar and the [M] used here was also low. The formation of stable five- or six-membered rings during cyclization is well known.[18,19] Mostly, DA and the quaternary ammonium salts (diallyldimethyl ammonium chloride) yield cyclopolymers consisting largely of five-membered rings.[21,22]

Under steady-state conditions, if the rate expression is derived with these possibilities, the rate equation would be

$$R_p = \sqrt{2(k_{21}/k_t^{1/2})k_0^{1/2}}[M][PMS]^{1/2}$$

where k_0 and k_t are the decomposition initiation rate constant and termination rate constant respectively.

This expression is in agreement with our experimentally observed dependence of R_p on [M] (Fig. 1) and [PMS]$^{1/2}$ (Fig. 2)

This rate expression can be verified for its fitness from the constancy in the composite rate constant [$k^* = (k_{21}/k_t^{1/2})k_0^{1/2}$]. k^* was obtained from the slope value of the plots (1) R_p versus [M] (Fig. 1) and (2) R_p versus [PMS]$^{1/2}$ (Fig. 2). The calculated k^* values were very close to one another (Table I). In the polymerization of AA and MMA in the presence of PMS and ultrasound, R_p followed a first-order dependence on AA/MMA and a half-order dependence on the initiator PMS, as in the DA–PMS system. Because these systems followed similar kinetic law, the decomposition rate (k_0) of PMS ($k_0 = 2.14 \times 10^{-4}\,s^{-1}$) observed in other systems[13,15] could be used in this system to determine the value of ($k_{21}/k_t^{1/2}$). The average $k_{21}/k_t^{1/2}$ values turned out to be 0.10 mol$^{-1/2}$ L$^{1/2}$ s$^{-1/2}$ for DA–PMS and 0.11 mol$^{-1/2}$ L$^{1/2}$ s$^{-1/2}$ for DA–PDS. It was clear that a similar reaction scheme was oper-

ical for the approach of the monomer and no pendant groups to prevent this propagation. The reaction at the position of the unreacted double bond of M_3 would then lead to crosslinking, as suggested by Buttler et al.[19] All reactions involving $M_3 \cdot$ and M_3 can be neglected because of the low probability of linear propagation and the production of pendant double bonds. In fact, the observed homogeneous polymerization under the reaction conditions and the absence of insoluble product led us to a mechanism without crosslinking.

A final picture of the propagation steps emerges from these considerations. The first step is the in-

TABLE I
Evaluation of Composite and Individual Rate Constants for the Polymerization of DA in the Presence of PMS and with Ultrasound at a Frequency of 1 MHz at 35°C

[DA] $\times 10^2$ (mol/L)	[PMS] $\times 10^4$ (mol/L)	Slope $\times 10^5$	$k^* \times 10^3$ (mol$^{-1/2}$/L$^{1/2}$/s^{-1})	$(k_{21}/k_t^{1/2})$ (mol$^{-1/2}$/L$^{1/2}$/s$^{-1/2}$)
Varied over the range 4–36	10.8	5.50 s^{-1}	1.67	0.11
	21.6	6.00 s^{-1}	1.29	0.09
20.0	Varied over the range 5–32	32.6 mol L$^{-1/2}$s^{-1}	1.63	0.11
11.8		16.0 mol L$^{-1/2}$–s^{-1}	1.36	0.09
			1.49[a]	0.10[a]

$k^* = (k_{21}/k_t^{1/2})k_0^{1/2}$
[a] Average value.

ating for both the systems in the propagation and termination reactions.

The $k_{21}/k_t^{1/2}$ values for various temperatures were calculated. From these values and from the slope of the Arrhenius plot, log $(k_{21}/k_t^{1/2})$ versus $1/T$, E_a for the propagation to the termination step was obtained. This was found to be 11 kJ/mol. From the Eyring plot, log $[(k_{21}/k_t^{1/2})/T]$ versus $1/T$, the change in enthalpy and entropy (ΔH and ΔS) values were obtained from the slope and intercept. These were found to be 11 kJ/mol and -62 J/°/mol, respectively. Similarly, E_a, ΔH and ΔS values are calculated for $k_{21}/k_t^{1/2}$ of the DA–PDS system.[16] They were 10.5 kJ/mol, 5.5 kJ/mol, and -63 J/°/mol, respectively.

We compared the thermodynamic properties of these two systems, DA–PDS and DA–PMS (Table II). E_a for the overall polymerization and the ratio of the rates of propagation to termination were different. The lower E_a for the propagation to termination step clearly indicated that this step took place at a faster rate before polymerization in both cases. This difference, moreover, reflected the involvement of the re-

TABLE II
Thermodynamic Parameters for Overall R_p and the Ratio of the Rates of Propagation to the Termination of DA with Peroxo Salts

	System		
	DA–PMS	DA–PDS	MAA–PMS
For overall polymerization			
E_a (kJ/mol)	44	31	19
ΔH (kJ/mol)	43	31	
ΔS (J/°/mol)	-31	-45	
For propagation to termination rate			
E_a (kJ/mol)	11	10.5	22
ΔH (kJ/mol)	11	5.5	20
ΔS (J/°/mol)	-62	-63	-66

spective initiation rate constant (k_0). However, the comparable E_a values of these systems for the propagation step suggested that cyclization followed by termination took place at a comparable rate because the $k_{21}/k_t^{1/2}$ values were constant. Such constant $k_{21}/k_t^{1/2}$ values obtained for these systems further supported our idea that propagation took place in a similar manner, that is, cyclization followed by termination. The different kinds of propagation in divinyl polymerization could also be visualized from the E_a values. The different E_a values (for the monovinyl monomer, MAA, $E_a = 22$ kJ/mol, and for the divinyl monomer, DA, $E_a = 11$ kJ/mol) suggested that different propagation pathways were followed in these steps. If there was linear propagation at all, as in the monovinyl polymerization (E_a for the overall polymerization and the propagation of the MAA–PMS system were in the same range, ~22 kJ/mol), the same E_a values would have been obtained for the DA–PMS system for polymerization and propagation. However, different E_a values for these steps, namely, polymerization (44 kJ/mol) and propagation (11 kJ/mol), further indicated the presence of different propagation pathways. Moreover, this difference also reflected the involvement of respective k_0 values of the initiators. However, the comparable E_a values of the DA–PDS and DA–PMS systems for propagation suggested that cyclization followed by termination took place at a comparable rate because the $k_{21}/k_t^{1/2}$ values were almost constant. Such constant $k_{21}/k_t^{1/2}$ values obtained for these two systems further supported our idea that propagation took place in a similar manner, that is, cyclization followed by termination. The difference in the k_0 values of PDS and PMS also could also be accounted for by the ΔH values of the overall polymerization and the ratio of propagation to termination rate constants. Again, that the ΔS values of these processes were almost constant but were less for the overall polymerization than for propagation indicated the participation of different k_0 values in addition to different ΔH values. Moreover, that the ΔH values of the DA–PMS

system were greater than those of the DA–PDS system for both the processes clearly reflected the presence of different initiation rate constants for different peroxo salts.

CONCLUSIONS

The polymerization of a symmetrical nonconjugated diolefin (DA) initiated by PMS occurred only in the presence of ultrasound. The experimental results suggest that intramolecular cyclization was followed by intermolecular propagation through a stable five-membered cyclized radical, which reacted with the monomers. The final product was a noncrosslinked water-soluble cyclopolymer.

References

1. Chandrasingh, U.; Manickam, S. P.; Venkatarao, K. Makromol Chem 1979, 180, 589.
2. Gopalan, A.; Paulrajan, S.; Vaidyanathan, S.; Venkatarao, K.; Subbaratnam, N. R. Eur Polym J 1984, 20, 971.
3. Manickam, S. P.; Venkatarao, K.; Subbaratnam, N. R. J Polym Sci Polym Chem Ed 1980, 18, 1679.
4. Subbaratnam, N. R.; Manickam, S. P.; Venuvanalingam, P.; Gopalan, A. J Macromol Sci Chem 1986, 23, 117.
5. Rathinamuthu, R.; Victoria, R.; Gopalan, A.; Vaidyanathan, S. J Polym Sci Part A: Polym Chem 1998, 36, 11.
6. Rathinamuthu, R.; Victoria, R.; Gopalan, A.; Vaidyanathan, S. Int J Polym Mater 1997, 38, 49.
7. Chindrella, L.; Gopalan, A.; Karthikeyan, G.; Subbaratnam, N. R. Polym Commun 1987, 28, 125.
8. Gopalan, A.; Paulrajan, S.; Subbaratnam, N. R. J Polym Sci Polym Chem Ed 1985, 23, 186.
9. Topchiev, D. A.; Bikasheva, G. T.; Martynenko, A. I.; Kaptsov, M. N.; Gudkova, L. A.; Kabanov, V. A. Vysokomol Soedin B 1980, 22, 269.
10. Chandrasingh, U.; Venkatarao, K. J Inorg Nucl Chem 1976, 38, 541.
11. Price, G. J.; Cliffton, A. A. Polym Commun 1996, 37, 3971.
12. Vivekanandam, T. S.; Gopalan, A.; Vasudevan, T.; Umapathy, S. Polym Commun 1999, 40, 807.
13. Vivekanandam, T. S.; Gopalan, A.; Vasudevan, T.; Umapathy, S. J Polym Sci Part A: Polym Chem 1998, 36, 2715.
14. Vivekanandam, T. S.; Gopalan, A.; Vasudevan, T.; Umapathy, S. J Polym Mater 1998, 15, 261.
15. Vivekanandam, T. S.; Gopalan, A.; Vasudevan, T.; Umapathy, S. J Appl Polym Sci 2000, 76, 524.
16. Vivekanandam, T. S.; Gopalan, A.; Vasudevan, T.; Umapathy, S. Eur Polym J 2000, 36,385.
17. Butler, G. B.; Ingley, F. I. J Am Chem Soc 1951, 73. 894.
18. Gibbs, W. E. J Polym Sci 1964, 2, 4815.
19. Butler, G. B. Cyclopolymerisation and Cyclocopolymerisation; Marcel Dekker: New York, 1992.
20. Butler, G. B.; Angelo, R. J. J Am Chem Soc 1957, 79, 3128.
21. Hawthrone, G. D.; John, S. R.; Solomon, D. H.; Willings, R. L. J Chem Soc Chem Commun 1975, 982; Aust J Chem 1976, 29, 1955.
22. Lancaster, J. E.; Baccei, I.; Panzer, H. P. J Polym Sci Polym Lett Ed 1976, 14, 549.