NOTES

Pyridinium Dicyanomethylide Initiated Copolymerization of Styrene and Methyl Methacrylate

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Polymer-ylide chemistry is a subject of growing interest. The work in this area was started mainly by Kondo et al.[1,2] and involved photolytic generation of radicals. This laboratory also had reported potential applications of nitrogen ylides[3-6] viz. picolinium and imidazolium as initiators for homo- and copolymerization of vinyl monomers.

Only a short time ago for the first time, the application of pyridinium dicyanomethylide as a radical initiator for homopolymerization of styrene (St) and methyl methacrylate (MMA) was reported by us.[7,8] In the present paper, the application of pyridinium dicyanomethylide (PDMY) to obtain the alternating copolymer of styrene with methyl metacrylate, even in the absence of a lewis acid otherwise essential for radical initiation, is reported for the first time.

EXPERIMENTAL

MMA and St were purified by washing with 4% NaOH and with distilled water to neutral and twice distilled before use. Purified solvents were used in the copolymerization. Tetracyanoethyleneoxide (Fluka AG No. 18509) and pyridine were used as such without further purification. The pyridinium dicyano-methylide, having following structure.
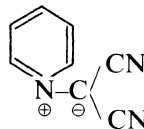
was prepared according to the method by Linn et al.[9] and was recrystallized twice with 50% ethanol–water mixture. It was insoluble in non-polar solvents like benzene and CCl_4 but soluble in polar solvents like dimethylformamide (DMF) and dimethylsulphoxide (DMSO) and had a high melting point[9] ($>250°C$).

A solution containing the requisitic quantities of ylide and monomers in DMF as an inert solvent was injected into a modified dilometric apparatus,[10] (0.2 mm capillary diam.). The reaction was carried out for 60 min at $85°C \pm 0.1°C$ under nitrogen atmosphere in order to keep the percentage conversion low. The progress of the reaction, monitored as meniscus movement per unit volume per unit time with the help of a cathetometer, was converted into percentage conversion. The copolymer, precipitated with acidified methanol, was then treated with acetonitrile and cyclohexane to remove homopolymers, wherein undetectable weight loss was noticed. The co-

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polymer so obtained was dissolved in benzene and reprecipitated with acidified methanol and then dried to a constant weight.

The rate of copolymerization (R_p) was calculated using the following equation[10]:

$$R_p(\text{mol}\,l^{-1}\,s^{-1}) = 0.7515 \times 10^{-3} \times \frac{U}{t} \quad (1)$$

where,

U = percentage conversion, and

t = polymerization time in minutes

The intrinsic viscosity $[\eta]$ of the copolymers, determined in toluene at 30°C using Ubbelohde viscometer, was converted to the average degree of polymerization ($\bar{P}_n$) as follows[10]:

$$[\eta] = 5.75 \times 10^{-3}\bar{P}_n\,0.746$$

NMR spectroscopy (Varian 100 HA spectrometer, CDCl$_3$ as the solvent and tetramethylsilane as the internal reference) has been used to characterize the copolymer.

RESULTS AND DISCUSSION

The results of radically initiated copolymerization of styrene and MMA are presented in Tables I—III and illustrated in Figures 1—4. The copolymerizations were associated with a short induction period (5—6 min).

Effects of Ylide

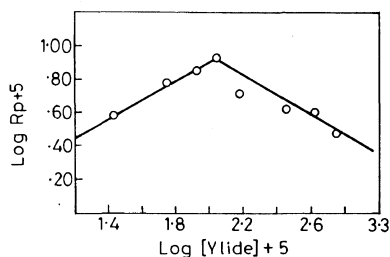A study of Table I reveals that the rate of copolymerization is a direct function of [Ylide]

Figure 1. Graph for log rate of copolymerization plotted against the log concentration of pyridinium dicyanomethylide. [MMA] = 1.44 mol l^{-1}; [St] = 1.38 mol l^{-1}; time = 60 min; temperature = 85°C ± 0.1°C.

from 2.7×10^{-4} to 11.1×10^{-4} mol l^{-1} but follows reverse suit thereafter upto 56.0×10^{-4} mol l^{-1} probably due to lower initiator efficiency which might be a consequence of primary radicals leading to their mutual annihilation to a certain extent. The order of

Table I. Copolymerization of styrene with MMA initiated by pyridinium dicyanomethylide[a]

Run No.	[Ylide] × 10^4 mol l^{-1}	Conversion percentage	R_p × 10^5 mol l^{-1} s^{-1}	$\bar{P}_n$
1	2.7	3.12	3.9	745
2	5.6	5.0	6.2	623
3	8.4	5.8	7.3	293
4	11.1	6.8	8.5	200
5	14.0	4.3	5.4	—
6	28.0	3.5	4.3	—
7	42.0	3.5	4.2	—
8	56.0	2.5	3.1	—

[a] [Styrene] = 1.38 mol l^{-1}; [MMA] = 1.44 mol l^{-1}; time = 60 min; temperature = 85°C ± 0.1°C.

Table II. Effects of [MMA] on the rate of copolymerization of styrene with MMA[a]

Run No.	[MMA] mol l^{-1}	Conversion percentage	R_p × 10^5 mol l^{-1} s^{-1}
1	0.36	1.24	1.5
2	0.72	2.4	3.0
3	1.08	3.17	3.9
4	1.44	4.3	5.4

[a] [Styrene] = 1.38 mol l^{-1}; [Ylide] = 14.0 × 10^{-4} mol l^{-1}; time = 60 min; temperature = 85°C ± 0.1°C.

Table III. Effects of [Styrene] on the rate of copolymerization of styrene with MMA[a]

Run No.	[Styrene] mol l^{-1}	Conversion percentage	R_p × 10^5 mol l^{-1} s^{-1}
1	0.34	1.2	1.5
2	0.69	2.3	2.9
3	1.04	3.1	3.9
4	1.38	4.3	5.4

[a] [MMA] = 1.44 mol l^{-1}; [Ylide] = 14.0 × 10^{-4} mol l^{-1}; time = 60 min; temperature = 85°C ± 0.1°C.
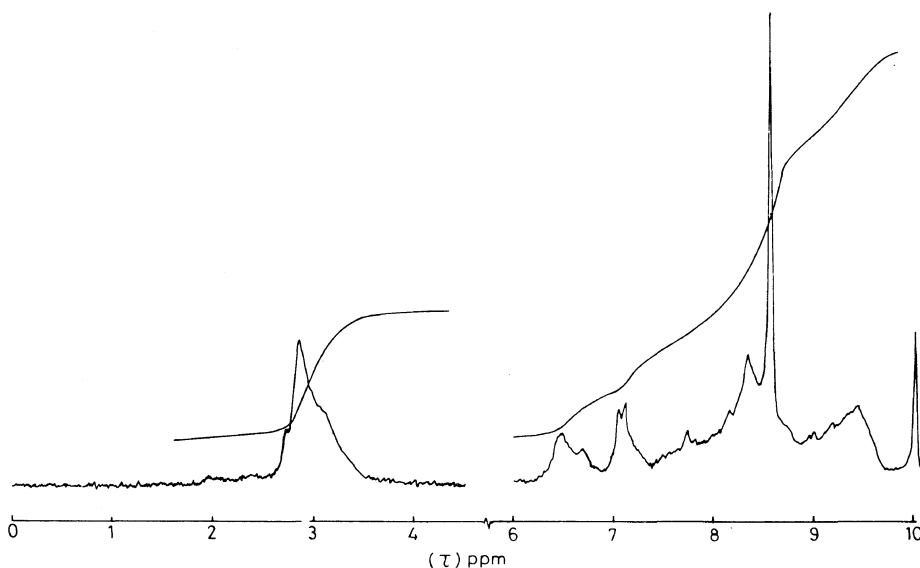
Figure 2. NMR spectrum of copolymer in CDCl₃. [Ylide] = 14.0×10^{-4} mol l^{-1}; [MMA] = 1.08 mol l^{-1}; [St] = 1.38 mol l^{-1}; time = 60 min; temperature = 85°C $\pm$ 0.1°C.
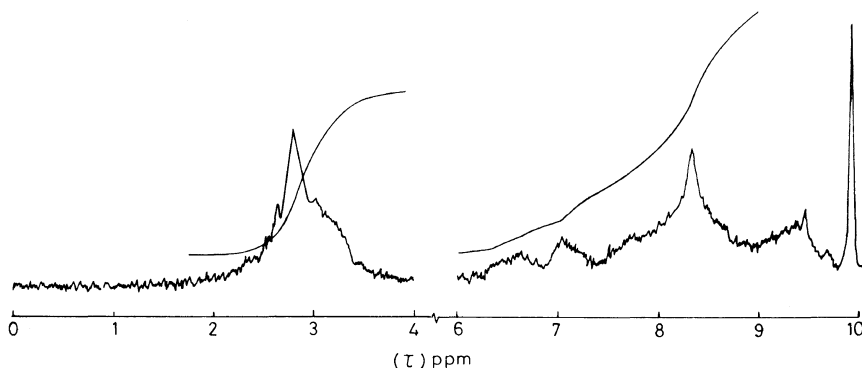
Figure 3. NMR spectrum of copolymer in CDCl₃. [Ylide] = 14.0×10^{-4} mol l^{-1}; [MMA] = 1.44 mol l^{-1}; [St] = 1.02 mol l^{-1}; time = 60 min; temperature = 85°C $\pm$ 0.1°C.

reaction with respect to initiator, calculated from the slope of linear plot of $\log R_p$ vs. log[Ylide] is 0.5 ± 0.02 (Figure 1).

The average degree of polymerization of copolymers decreases with increasing initiator concentration, as expected for radical polymerization. The initiator exponent value and absence of an intercept in the plot of $1/\bar{P}_n$ vs. [Ylide]$^{0.5}$ suggest that free radical polymerization with bimolecular termination takes place.

The value of k_p^2/k_t, evaluated from slope of linear plot of $1/\bar{P}_n$ vs. R_p is 8.0×10^{-4} l mol^{-1} s^{-1}.

Effects of Monomers

The effects of [Monomers] on the R_p have also been studied and the results are summarized in Tables II and III. The monomer exponent values calculated from the slope of linear plot of $\log R_p$ vs. log[Monomer] is unity for both MMA and St.
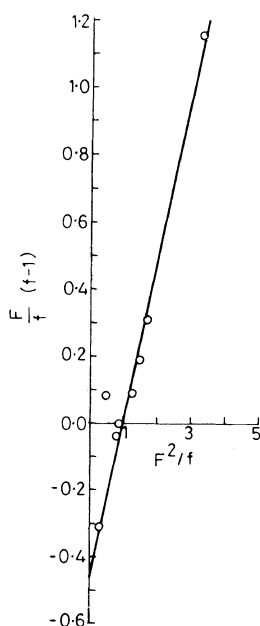
Figure 4. Finemann–Ross lower case.
$F=[St]/[MMA]$
$f=M_1/M_2$ where M_1 [St] and M_2 [MMA] refer to the compositions of monomer in mole fractions calculated as from the NMR spectrum of the copolymer.

Effects of Hydroquinone

The initiator and monomer exponent values clearly suggest the radical mode of copolymerization, which is further confirmed by effects of hydroquinone on the copolymerization. The effects of hydroquinone have been studied by varying [hydroquinone] from 3.6×10^{-3} mol l^{-1} to 7.2×10^{-3} mol l^{-1}. For this change, R_p decreases from 5.4×10^{-5} mol l^{-1} s^{-1} to 1.2×10^{-5} mol l^{-1} s^{-1}. The copolymerization was inhibited when [hydroquinone] was raised to 9.0×10^{-3} mol l^{-1}.

Effects of Temperature

The rate of copolymerization increases with increase in polymerization temperature. The energy of activation (ΔE) for the system, calculated from the linear Arrhenius plot is 96 kJ mol^{-1}.

Structure and Composition

NMR spectroscopy has been used to characterize the copolymers of styrene and MMA. The NMR spectra are shown in Figures 2 and 3. There are five main resonance peaks observed. The singlet at 2.9—3.4τ is due to a phenyl proton of the styrene unit. The methyl protons appear at 9.2—9.6τ, the methoxy protons at 6.4—6.8τ, 7.1—7.3τ, and about 7.8τ, which overlap in the region of 8.0—8.8τ due to methylene and methyne protons. These three methoxy peaks are assigned[11] to cosyndiotactic (6.6τ), coheterotactic (7.1τ), and coisotactic (7.8τ) triad from low to high field. The appearance of methoxy protons as three splitted peaks suggests that the copolymer, prepared with the help of pyridinium dicyanomethylide has an alternating nature because in the case of random copolymers, the methoxy protons appear as a singlet peak at 6.38τ.[11] The relative areas due to phenyl protons of styrene and methoxy protons of MMA permit us to calculate copolymer composition.

Reactivity Ratios

The Finemann–Ross method[12] has been used to estimate the reactivity ratios from copolymer composition data.

The values of r_1 (St) and r_2 (MMA) (Figure 4) were found to be 0.46 and 0.45, respectively, which match well with those reported in the literature[13] thereby confirming alternating nature of the copolymers.

CONCLUSIONS

On the basis of the above discussion, it may be concluded that pyridinium dicyanomethylide can be used as a radical initiator to obtain an alternating copolymer of styrene and methyl methacrylate even in the absence of a Lewis acid.

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