Grafting. III. Copolymerization of Methyl Methacrylate and Methacrylic Acid

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Synopsis

The method of graft copolymerization of methyl methacrylate on halogen-containing polymer has been utilized for grafting of methyl methacrylate–methacrylic acid monomer pair onto poly(vinyl chloride) and chlorinated rubber. Substantial grafting could be obtained by using the method reported earlier. However, the compositions of the grafted chains are found to deviate appreciably from the compositions calculated from r_1 and r_2 values reported in literature. The reactivity ratios for this pair of monomers have been therefore evaluated using azobisisobutyronitrile and *n*-butane thiol–dimethyl sulfoxide as initiators. The anomalies of the grafted chain compositions have been discussed and an explanation presented on preferential solvation.

INTRODUCTION

Synthesis of thiolated polymers from poly(vinyl chloride) and grafting of monomers onto these polymers have been reported earlier.[1] It was found that the initiator system comprising thiol–dimethyl sulfoxide (DMSO) is monomer specific. Thus methyl methacrylate (MMA) could be successfully grafted, but styrene and vinyl acetate responded poorly.[2] Similar behavior was observed for methacrylic acid (MAA). Since the present catalyst was efficient for MMA, it would be interesting to initiate graft copolymerization with mixed monomer system containing methyl methacrylate as one component. The thiol–DMSO pair is utilized only for the generation of free radical. The composition of the copolymer branches in graft copolymers, therefore, should correspond to that obtained with conventional catalyst system such as azobisisobutyronitrile (AIBN). Literature on copolymer compositions and reactivity ratios for MMA–MAA system is rather scanty and indications are that the reactivity ratios as well as rates of polymerization are sensitive to the presence of other ingredients such as solvent and chain transfer agent.[3] Explanation of these factors is mostly attempted on the basis of complex formation between methacrylic acid and its radical with the polar components present in the system.[4]

In this communication, an attempt has been made to graft copolymerize MMA and MAA on poly(vinyl chloride) (PVC) and chlorinated rubber (CLR). Simple binary copolymerization of MMA and MAA has also been carried out

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over a wide range of monomer feed compositions to ascertain the reactivity ratios and compare with the data available in literature.

EXPERIMENTAL

Purification of MMA was done as reported previously.[1] Inhibited MAA was repeatedly recrystallized at 13.5°C and the recrystallized product was fractionally distilled under a reduced pressure of N_2 using a condenser packed with Cu foils to avoid thermal polymerization. The distilled monomer was stored at $-15°C$.

PVC (NOCIL, India) and CLR (Rishiroop Chemicals, India, chlorine content ≈ 64%) were purified by precipitation from methyl ethyl ketone and benzene solutions, respectively, using methanol as nonsolvent. The polymers were then dried at 50°C under reduced pressure. The polymers have viscosity average molecular weights of 31,000 and 63,000, respectively.

Analytical grade DMSO, n-butane thiol, and solvents were used as such without further purification. AIBN was recrystallized thrice from alcohol and dried in cold under vacuum.

Graft Copolymerization

Thiolation of PVC and CLR was carried out by using H_2S in alkaline alcoholic medium. The extent of thiolation was estimated using the method of Doly et. al.[5] Grafting of MMA–MAA mixture on thiolated polymer was done as reported earlier[1] and copolymerization was conducted to a conversion of about 5%. The polymers were dissolved in tetrahydrofuran and precipitated in cyclohexane. The dissolution precipitation was followed thrice and final two precipitations were carried out using aq. methanol as nonsolvent. The copolymers were dried at 50°C under reduced pressure to constant weight. The compositions of the graft copolymer were ascertained from chlorine and carboxylic acid contents.

Copolymerizations of MMA–MAA Mixtures

Two series of copolymerizations covering the entire range of monomer feed compositions were conducted using AIBN and thiol–DMSO initiator systems. The ampoules containing the monomer mixtures were freeze-thawed repeatedly and then sealed. After specified periods of polymerization (conversion not exceeding 5%), the ampoules were cut open and the contents precipitated in cyclohexane. The polymers were dissolved in tetrahydrofuran, reprecipitated in excess aqueous methanol, and dried to constant weight at 50°C under reduced pressure. The compositions of the copolymers were determined in aqueous alcohol in the presence of potassium nitrate by potentiometric titration.

Copolymerizations using three monomer feed compositions of MMA–MAA were also carried out with AIBN and DMSO–thiol in the presence of nonactivated poly(vinyl chloride) and chlorinated rubber.

RESULTS AND DISCUSSION

Table I shows the composition of graft copolymers corresponding to specific monomer feed composition (corresponding to 50:50 w/w of monomers in

TABLE I
Graft Copolymer Compositions for PVC–MMA–MAA and CLR–MMA–MAA System at 60°C in Cyclohexanone

Backbone polymer	Feed composition	Copolymer composition, experimental (wt %)	Grafting efficiency (%)	Grafted chain composition (mole fraction of MMA and MAA)	
				Experimental	Theoretical
1. Thiolated PVC (Thiol equivalent = 2840)	Polymer: 20 gm L^{-1} MMA: 0.9 mol L^{-1} MAA: 1,16 mol L^{-1} DMSO: 0.5 mol L^{-1}	PVC: 40.2 PMMA: 37.7 PMAA: 22.1	150	$F_{MMA} = 0.595$ $F_{MAA} = 0.405$	$F_1 = 0.289$[a] 0.514[b] $F_2 = 0.711$ 0.486
2. Thiolated chlorinated (Thiol equivalent = 4700)	Polymer: 37.5 g L^{-1} MMA: 1.8 mol L^{-1} MAA: 2.3 mol L^{-1} DMSO: 0.5 mol L^{-1}	Chlorinated rubber: 32.6 PMMA: 41.8 PMAA: 25.6	236	$F_{MMA} = 0.584$ $F_{MAA} = 0.416$	$F_1 = 0.289$[a] 0.514[b] $F_2 = 0.711$ 0.486

[a] Using $r_1 = 0.30$, $r_2 = 1.6$.[3]
[b] Using $r_1 = 1.18$, $r_2 = 0.63$.[3]

copolymer). The composition of the grafted chains is found to be substantially different from that obtained using values of reactivity ratios (r_1 and r_2) reported in the literature with the help of the following equation:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{1}$$

where the symbols have their usual meaning. However, copolymer compositions calculated using r_1 and r_2 values for systems involving chain transfer agent are closer to the values experimentally found in the present system. Nevertheless, it is clear that MAA contents in the grafted chains are lower than expected on the basis of available literature values of r_1 and r_2.

The present study includes DMSO as one component of the initiator system, which is known to form strong hydrogen bond with methacrylic acid. The presence of adventitious sulfoxide in the polymer would result in an underestimation of the acid component as any adhering sulfoxide is weighed in favor of MMA. The graft copolymers were therefore stringently purified and the presence of DMSO was checked at each stage of purification. Initial precipitations showed a distinct peak of DMSO at 1000–1035 cm^{-1} due to S=O stretching. On subsequent precipitation, the same peak disappeared, showing no contamination. Compositional analysis presented in Table I is based on data utilizing the purified polymers. It thus seems reasonable to conclude that introduction of acid component in the grafted chain is impeded compared to purely binary copolymerization.

Copolymerization of MMA and MAA has been reported by a few[6-8] and there is considerable difference between the values of reactivity ratios of various workers. Recently Bajoras and Makuska[4] reported on anomalous behavior in the homo- and copolymerizations of MAA in the presence of DMSO. It was observed in confirmity to our results that the rate of addition of MAA to its own radical and to other monomer radicals decreases appreciably in the presence of DMSO. The authors attributed this decrease to a complex formation between MAA and DMSO, resulting in high electron density on the former. However, the acid radical in the complex form should be highly reactive. A decreased probability of π complex formation of the radical was suggested by Bajoras and Makuska to account for the decreased rate.

In view of the disparity between grafted chain compositions and the theoretically calculated values, it was considered necessary to study in detail the binary copolymer compositions of MMA–MAA mixtures prepared using a conventional initiator AIBN and n-butane thiol–DMSO systems. The concentrations of both AIBN and thiol–DMSO have been kept constant for the entire monomer feed ratio. The copolymer compositions for both the initiator systems were treated according to the Kelen–Tudos[9] equation

$$\frac{G}{\alpha + F} = \left(r_1 + \frac{r_2}{\alpha} \right) \frac{F}{\alpha + F} - \frac{r_2}{\alpha} \tag{2}$$

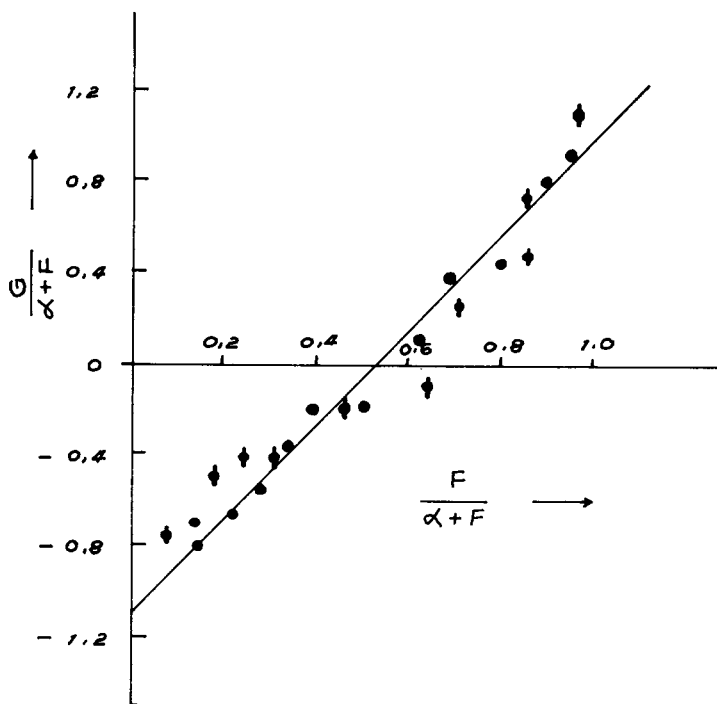where α is an arbitrary constant, preferably equal to $\sqrt{(F_M F_m)}$, F_M and F_m

Fig. 1. Kelen–Tüdos plot for copolymerization of methyl methacrylate and methacrylic acid in cyclohexanone at 60°C initiated by: (●) [AIBN] $(10^{-3}$ mol $L^{-1})$; (●) n-butanethiol–DMSO mixture. [Thiol] $= 1.10^{-3}$ mol L^{-1}, [DMSO] $= 5 \times 10^{-1}$ mol L^{-1}; α = arbitrary constant; $F = x^2/y$ and $G = x - (1/y)$, where x = ratio of moles of monomer in feed and y = ratio of moles of monomer in polymer formed.

being the maximum and minimum values of F in a given set of experimental data. Figure 1 shows plots corresponding to eq. (2) for MMA–MAA–AIBN and MMA–MAA–thiol–DMSO systems. The experimental data for both the systems could be represented by a single straight line within experimental error. Values of r_{MMA} and r_{MAA} calculated are 1.00 ± 0.050 and 0.44 ± 0.025, respectively. Since both AIBN and thiol–DMSO initiator systems give the same values of reactivity ratios, it can be concluded that the reactivities of both methacrylic acid and its radical remain unaffected when DMSO is present to the extent of about 0.5 mol L^{-1}. If the reactivities of both the acid and the radical are assumed to be considerably decreased as a result of complexation, k_{22} should be drastically reduced resulting in a very low value of r_2 $(= k_{22}/k_{21})$. Moreover, the effect on composition should be more pronounced at low acid concentrations when most of the acid will be in the complexed form. The results thus indicate that the presence of DMSO in the concentration of about 0.5 mol L^{-1} does not affect the copolymerization behavior of the MMA–MAA mixture and that the results are in good agreement with those obtained using AIBN.

To examine the effect of addition of small amounts of DMSO on copolymerization of MMA–MAA with AIBN, experiments were carried out with three monomer feed compositions containing appreciably high MAA. Figure 2 shows copolymer compositions vs. the monomer feed composition for
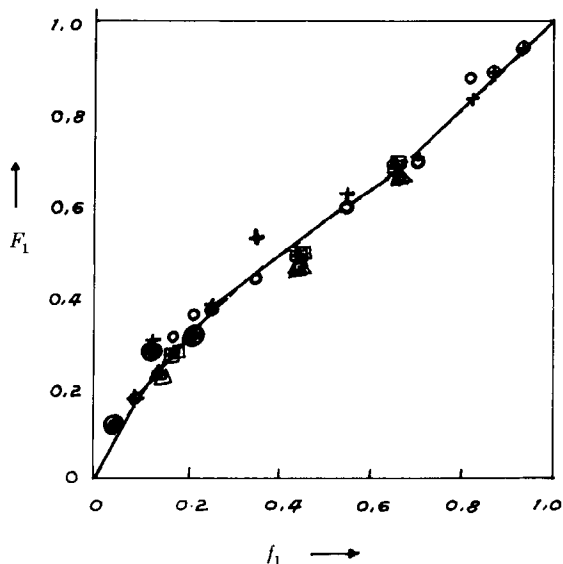
Fig. 2. Copolymer composition vs. monomer feed composition for MMA–MAA copolymeriza-
tion in cyclohexanone at 60°C initiated by: (○) [AIBN] (10^{-3} mol L^{-1}); (+) n-
butanethiol–DMSO mixture; ([thiol] = 1 × 10^{-3} mol L^{-1}, [DMSO] = 5 × 10^{-1} mol L^{-1}); (⊙)
AIBN–DMSO mixture; ([AIBN] = 10^{-3} mol L^{-1}, [DMSO] = 5 × 10^{-1} mol L^{-1}); (△) AIBN in
the presence of nonactivated PVC; (▲) AIBN in the presence of nonactivated chlorinated rubber
([AIBN] = 10^{-3} mol L^{-1}); (□) DMSO–thiol in the presence of nonactivated PVC; (▣)
DMSO–thiol in the presence of nonactivated chlorinated rubber. [Thiol] = 1.10^{-3} mol L^{-1};
[DMSO] = 5 × 10^{-1} mol L^{-1}; F_1 = mole fraction of M, in polymer formed; f_1 = mole fraction
of M, in monomer feed.

MMA–MAA–AIBN, MMA–MAA–butane thiol–DMSO in cyclohexanone at
60°C. The solid line represents the theoretical curve with $r_1 = 1.0$ and $r_2 = 0.44$. As is seen, experimental points could be well described by the reactivity
ratios determined. The three compositional points for MMA–MAA–AIBN–
DMSO are also presented in the same figure. It is evident that the same
reactivity ratios can describe these three points clearly. Thus it can be
concluded that addition of a small amount of DMSO in a normal MMA–MAA
copolymerization system does not alter the main features of the reaction. The
three experimental points for each system, MMA–MAA–AIBN and
MMA–MAA–n-butane thiol, in the presence of nonactivated PVC and chlori-
nated rubber are also shown in Figure 2. It is evident that the compositions of
the copolymers are very well covered by the r values of the copolymerization
system in absence of added polymer. This points to the fact that the nonacti-
vated backbone polymers do not affect the course or kinetics of copolymeriza-
tion.

    The effect of thiol in the copolymerization has not been studied in view of
the fact that it is fixed on the main chain of the backbone polymer and
secondly its concentration is of the order of about 7 × 10^{-3} mol L^{-1}. Earlier
experience[2] has shown that most of the thiol groups are utilized as initiating
centers and chain transfer to MMA does not affect its homopolymerization
behavior. On the other hand, MAA could not be grafted using the
thiol–DMSO system, even though the generation of free radical could be

detected by decoloration of Vardaxyl. Considering these facts, it seems unlikely that the bound thiol would alter the reactivity ratios to a detectable extent.

Referring back to Table I and considering the values of r_1 and r_2 determined, it is evident that the discrepancies between grafted chain composition and normal copolymer composition could not be explained on the basis of complexities introduced by thiol or DMSO. It seems logical to consider a situation where like pair contact is more favorable. Chlorinated rubber or PVC is much less polar compared to MAA. However, MMA is more compatible to both these polymers than MAA, as reflected in the values of cohensive energy densities. In a solution containing the polymer (either PVC or CLR), MMA and MAA, the polymer will be preferentially surrounded by MMA rather than MAA. Since the initiating free-radical centers are located on the backbone polymer, there is a preponderance of addition of MMA than MAA, at least in the initial stages of chain growth. Since a branched or a graft polymer has a tendency to attain more compact structure, the growing branches may rarely be in the vicinity of the monomer feed composition. The composition corresponding to r_1 and r_2 values of simple binary copolymerization may never attain in the grafted chains. The concept of preferential solvation of the backbone polymer by MMA seems to qualitatively explain the anomalous grafted chain composition observed in the present study. However, no quantitative assessment seems possible at this stage. The concept of "bootstrap model" put forward by Harwood[10] is relevant in this context. It has been argued that the concentration of monomers and the ratio of the monomer concentrations which govern the addition of the particular monomer on growing copolymer chain may not be the same throughout. These parameters may be different in the vicinity of a growing chain compared to the compositions charged to the polymerization system. For each growing branch in the graft copolymerization, the initial growing site itself resembles a growing macroradical. It thus seems reasonable to contend that graft copolymerization with proper selection of polymer may offer a possibility of judging the applicability of the "bootstrap" model. However, it may be pointed out here that, in the present system, the backbone polymer is relatively more compatible with one of the monomers (MMA) and hence preponderance of this monomer in the vicinity of the growing radical at least initially seems to be a distinct possibility. Studies on the positional arrangements of the monomers in the grafted chain would definitely have far-reaching implications which will be attempted.

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