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CHARACTERISTICS OF HETEROPHASE GRAFT COPOLYMERIZATIONS†

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ABSTRACT

Persulfate-initiated graft copolymerizations of glutaraldehyde crosslinked gelatin with acrylic acid, acrylamide, vinyl acetate, and methyl methacrylate in the aqueous phase were investigated. It was observed that percentage grafting, molecular weights of the grafts, and grafting efficiencies were greatly influenced by the nature of the monomers. Hydrophilic monomers gave a higher frequency of grafting but lower molecular weights. While the frequency of grafting with hydrophobic monomers was low, the molecular weights of the grafts were comparatively high. The results are explained in terms of microdomain kinetics, similar to those encountered in emulsion or suspension polymerizations.

INTRODUCTION

The kinetics of heterophase reactions are decidedly different from homogeneous reactions. The surface area exposed to the reactants together with the swelling characteristics of the insoluble component in the reaction medium is of prime significance in any heterophase process. Consequently, when grafting onto insoluble matrices is considered, the extent to which the matrix can imbibe the monomer and initiator influences the onset of initiation and the progress of grafting. The swelling characteristics of the grafted matrix are equally important from the point of view of propagation and termination steps. If the grafted matrix can absorb the mono-

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mer and initiator fragments equally well, then the propagation and termination reactions will be competitive. If, however, there is preferential uptake of monomer alone, then the propagation proceeds smoothly, yielding unusually high molecular weight grafts. In addition, these chain transfer reactions can greatly influence the course of polymerizations.

Glutaraldehyde crosslinked gelatin is a biodegradable matrix suitable for a variety of applications. However, it has very limited swellability in water and none in a nonaqueous medium. Graft copolymerization with suitable monomers can greatly improve the swelling properties of this matrix [1-3]. In an earlier report [1] we discussed the preparation and properties of gelatin with hydrophilic/hydrophobic grafts and glutaraldehyde crosslinks. Subsequently, we briefly investigated the grafting kinetics of the crosslinked gelatin-*g*-polyacrylamide system [2] and the polymethyl acrylate system [3].

Here we present an analysis of the graft copolymerization of crosslinked gelatin with acrylic acid, acrylamide, vinyl acetate, and methyl methacrylate (MMA). The salient feature of these grafting reactions is essentially the swelling characteristics of glutaraldehyde crosslinked gelatin. While the water-soluble monomers can freely diffuse into the matrix, vinyl acetate and methyl methacrylate face a barrier due to their negligible solubility (vinyl acetate 1-2% and MMA 1-1.5% at 20°C in water). This difference expresses itself in the percentage grafting, grafting efficiency, and molecular weights of the grafts.

MATERIALS AND METHODS

Gelatin, glutaraldehyde (25% aqueous solution), and acrylamide were supplied by Loba Chemicals, Bombay. Potassium persulfate (BDH) and A.R. grade solvents were used as such. The other monomers were purified according to standard procedures [4]. All reactions were carried out in oxygen-free distilled water.

The abbreviations used are given in Table 1.

TABLE 1. Abbreviations and Symbols Used

GLA	Glutaraldehyde
Gelx	Crosslinked gelatin
AA	Acrylic acid monomer
Aam	Acryl amide monomer
MMA	Methyl methacrylate
VAC	Vinyl acetate monomer
KPS	Potassium persulfate
PAA	Polyacrylic acid
PMMA	Polymethyl methacrylate
Gelx-*g*-PAA	Poly(acrylic acid)-grafted crosslinked gelatin
Gelx-*g*-PMMA	Poly(methyl methacrylate)-grafted crosslinked gelatin
C_M	Chain transfer constant to the monomer

Preparation of Gelx

Gelatin granules were crosslinked with 1% glutaraldehyde as described earlier [1].

Graft Copolymerizations

Reaction flasks with specified quantities of Gelx, monomer, and KPS in water were kept in a thermostat to ensure uniform conditions. To end the reaction, the system was first quenched with hydroquinone. The reaction mixture was then extracted exhaustively with a suitable solvent in a Soxhlet unit for the separation and quantitative estimation of the graft copolymer and homopolymer. The homopolymer was precipitated from the Soxhlet extract by using a suitable nonsolvent. The graft copolymers and homopolymers were dried at 40°C under vacuum until the weights were constant.

The percentage grafting, grafting efficiency, and percentage conversion were calculated as follows:

$$\text{percentage grafting} = 100 \times \frac{\text{weight of polymer grafted}}{\text{weight of Gelx}}$$

$$\text{grafting efficiency (\%)} = 100 \times \frac{\text{weight of polymer grafted}}{(\text{weight of polymer grafted} + \text{weight of homopolymer})}$$

$$\text{total monomer conversion (\%)} = 100 \times \frac{(\text{weight of polymer grafted} + \text{weight of homopolymer})}{\text{weight of monomer taken}}$$

The grafts were stripped from the Gelx matrix by acid hydrolysis [5]. Their average molecular weights were estimated either by viscosity or GPC methods. For molecular weight determinations by viscosity methods, the relevant equations and constants were obtained from the literature [6].

RESULTS AND DISCUSSIONS

Gelatin can be crosslinked at room temperature with aqueous GLA solution [1, 7]. The crosslinking is little more than a simple aldimine formation between the ϵ amino groups of the lysine residues of the protein and the aldehyde functionality of GLA [8]. GLA is largely polymeric and contains significant amount of α–β unsaturated aldehydes as aldol condensation products. These can give rise to Michael-type adducts which will be stable to even acid hydrolysis.

Crosslinked gelatin is insoluble in water but can swell appreciably, the swellability being a function of the extent and conditions of crosslinking [9]. Solution crosslinked networks can swell many times more than solid-state crosslinked samples. Figure 1 gives the swelling pattern of solution crosslinked gelatin as a function of concentration.

In our study the Gelx granules are dispersed in an aqueous medium with an initiator soluble in water. Acrylic acid and acrylamide, both being water soluble, can freely diffuse into the matrix. The high local concentrations of these ingredients could create a favorable environment for grafting. This is not the case with either vinyl acetate or methyl methacrylate. The grafting has to be initiated at the inter-

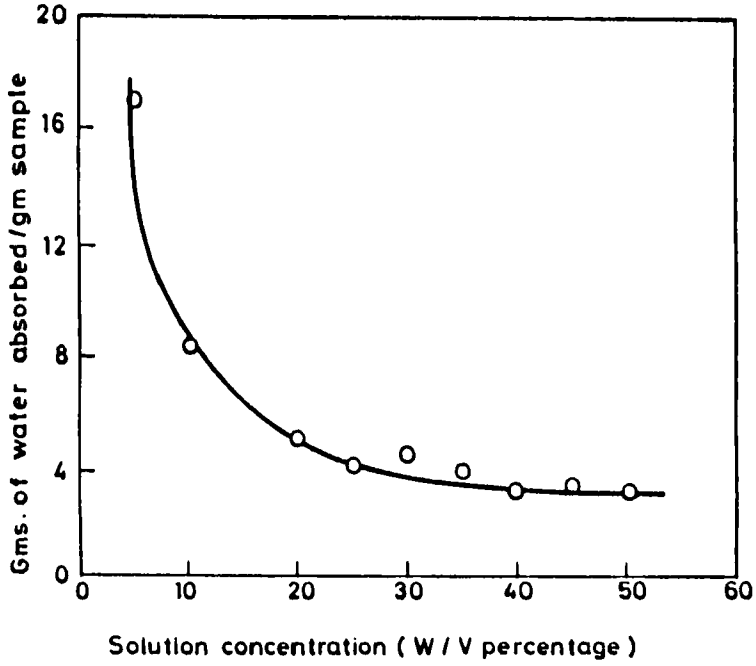

FIG. 1. Swelling characteristics of crosslinked gelatin in water.

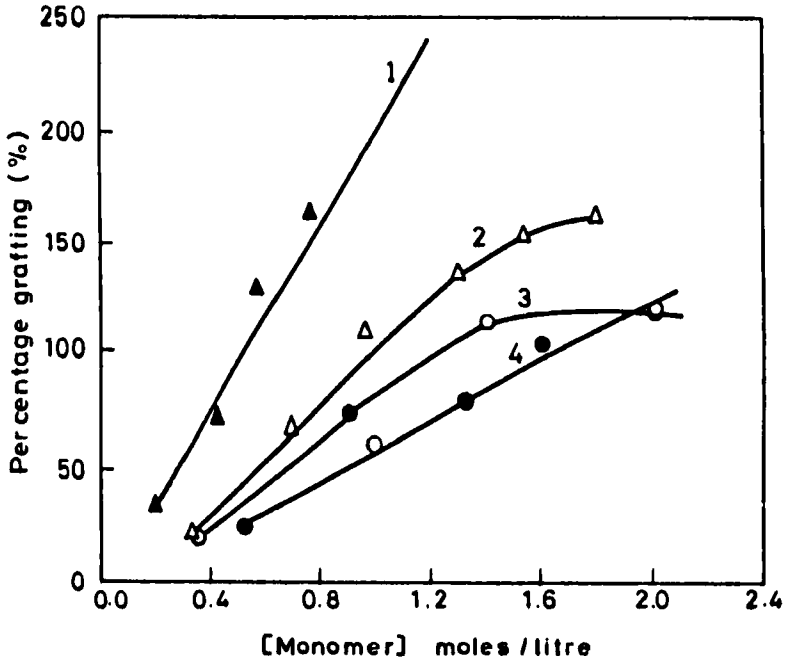

FIG. 2. Effect of monomer concentration on percentage grafting. 1: Monomer [MMA], [KPS] = 7.5 mmol/L. 2: Monomer [AA], [KPS] = 7.5 mmol/L. 3: Monomer [Aam], [KPS] = 9.25 mmol/L. 4: Monomer [VAc], [KPS] = 22.0 mol/L. Grafting conditions: Gelx = 1 g, 65°C, aqueous phase = 20 mL.

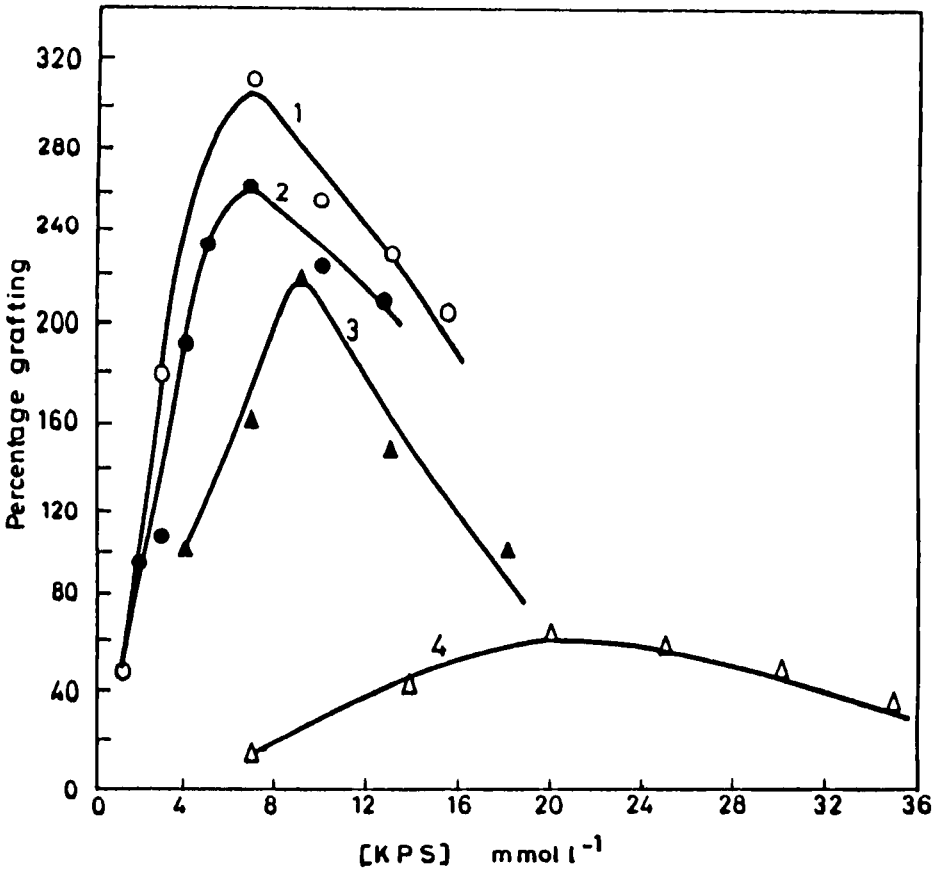

FIG. 3. Effect of KPS concentration on percentage grafting. 1: [AA] = 72.9 mmol. 2: [MMA] = 47.0 mmol. 3: [AAam] = 70.0 mmol. 4: [VAc] = 54.0 mmol. Grafting conditions: Gelx = 1 g, aqueous phase = 20 mL, 65°C.

phase of the Gelx granule–monomer droplet. This fundamental difference influences the initiation, propagation, and termination processes.

Figure 2 projects the influence of monomer concentrations on grafting. While acrylic acid and acrylamide tend toward saturation values, vinyl acetate and methyl methacrylate behave differently. The percentage grafting registers a steady increase within the same concentration range. It is possible that at still higher concentrations the values may reach the plateau. However, there are practical difficulties in exploring these concentration ranges due to excessive gelling/precipitation. The corresponding values of grafting efficiency and percentage conversion are given in Fig. 5.

The profiles of percentage grafting with respect to initiator concentration pass through a maximum for all monomers although the exact values vary (Fig. 3). This is in accordance with the general rules of polymerization kinetics [10]. Besides, acrylamide and vinyl acetate require higher concentrations of KPS for efficient grafting (Fig. 6).

The dependence of percentage grafting efficiency and percentage conversion on time are given in Figs. 4 and 7. Interestingly, except for acrylic acid, the monomers show an induction period. It appears that the creation of active centers on the Gelx passes through an initial sluggish phase; conditions are more favorable for homopolymerization. However, once the sites are created, the grafting competes with homopolymerization. Figure 7, where we have plotted grafting efficiency as a function of time, illustrates this point. Longer times do not seem to favor higher percentages of grafting. The rapid depletion of the monomer and the increasing viscosity of the medium might be responsible for this [2].

The Dilution Factor

Since gelling (in the case of acrylic acid and acrylamide) or precipitation (vinyl acetate and methyl methacrylate) occur with the progress of the polymerization, very low and very large volumes were found to be unfavorable for grafting [2]. At low volumes the matrix suffers constraints to swelling, and at high dilutions the effective concentrations of the monomer/initiator are so low that the grafting percentage invariably falls (Fig. 8).

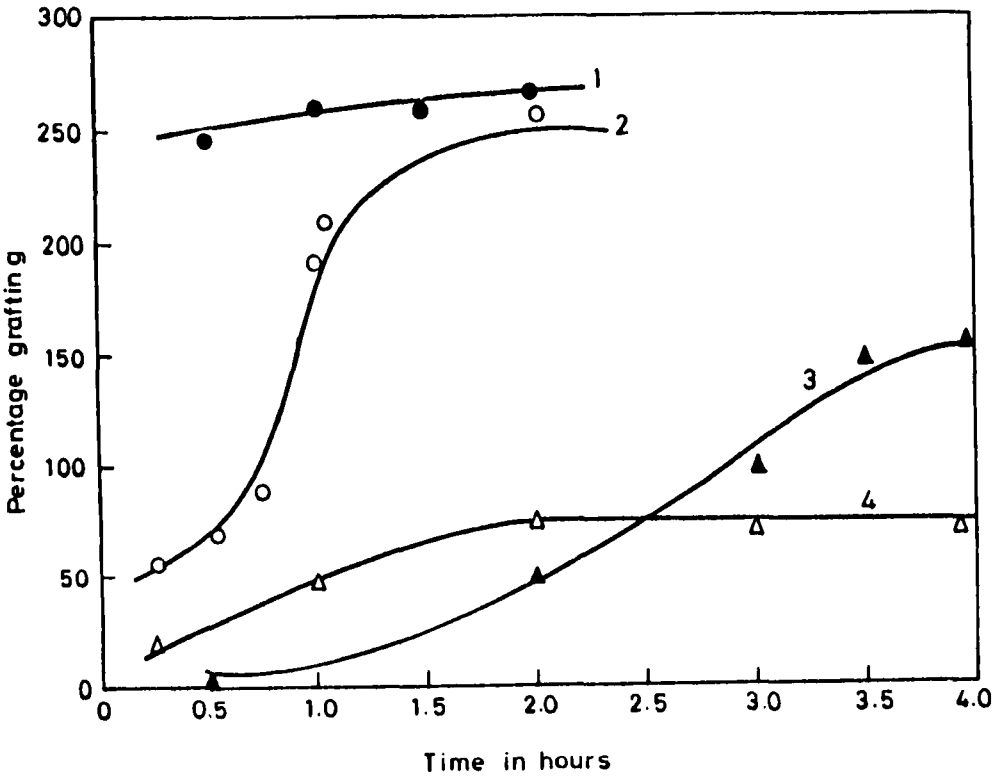

FIG. 4. Effect of time on percentage grafting. 1: [AA] = 72.9 mmol, [KPS] = 9.25 mmol/L. 2: [MMA] = 47.0 mmol, [KPS] = 9.25 mmol/L. 3: [Aam] = 70.0 mmol, [KPS] = 9.25 mmol/L. 4: [VAC] = 54.0 mmol, [KPS] = 27.74 mmol/L. Total volume = 20 mL, 65°C.

TABLE 2. Molecular Weight Profiles of Grafts and Grafting Frequencies: (Gelx-*g*-PAA) System

No.		Percentage of grafting	Average molecular weight of grafts	Moles of PAA grafted per mole of gelatin	Specifications
			Effect of Monomer Concentration		
	AA (mmol)				
1	21.8	107.7	6.2×10^3	69.66	[Gelx] = 1 g
2	29.1	135.4	6.66×10^3	81.9	[KPS] = 1.84×10^{-4} mol
3	36.4	151.5	1.21×10^4	50.45	[Water] = 20 mL
4	43.7	154.5	8.88×10^3	70.11	[Temp] = 70°C
			Effect of Initiator Concentration		
	KPS (mol)				
1	1.10×10^{-4}	160.6	1.65×10^4	39.0	[Gelx] = 1 g
2	1.47×10^{-4}	175.2	1.34×10^4	52.6	[AA] = 0.0729 mol
3	1.84×10^{-4}	203.3	1.17×10^4	70.02	[Water] = 20 mL
4	2.77×10^{-4}	215.2	1.27×10^4	68.28	[Temp] = 70°C
5	3.69×10^{-4}	217.2	1.62×10^4	54.03	
			Effect of Dilution		
	Volume (mL)				
1	10	314.4	2.07×10^4	61.1	[Gelx] = 1 g
2	25	171.1	1.30×10^4	53.04	[KPS] = 1.84×10^{-4} mol
3	40	167.6	9.7×10^3	69.2	[AA] = 0.0729 mol
4	50	70.3	8.67×10^3	32.6	[Temp] = 70°C
5	75	86.2	5.63×10^3	61.7	
			Effect of Reaction Time		
	Time (min)				
1	15	281.7	9.87×10^3	115.02	[Gelx] = 1 g
2	30	281.0	8.52×10^3	132.9	[KPS] = 1.84×10^{-4} mol
3	60	282.7	1.07×10^4	106.2	[AA] = 0.0729 mol
4	90	282.7	7.16×10^3	160.2	[Water] = 20 mL
5	120	279.1	1.16×10^4	97.0	[Temp] = 70°C

TABLE 3. Molecular Weights of Grafts and Grafting Frequencies: (Gelx-*g*-PMMA) System

No.		Percentage of grafting	Average molecular weight of grafts	Moles of MMA grafted per mole of gelatin	Specifications
			Effect of Monomer Concentration		
	MMA (mmol)				
1	4.71	31.8	7.56×10^4	1.695	[Gelx] = 1 g
2	9.43	74.5	4.09×10^5	0.732	[KPS] = 1.84×10^{-4} mol
3	18.86	164.5	4.44×10^5	1.49	[Water] = 20 ml
4	28.2	237.9	5.40×10^5	1.773	[Temp] = 70°C
5	37.7	291.5	7.70×10^5	1.523	
6	47.1	340.6	5.57×10^5	2.463	
			Effect of Initiator Concentration		
	KPS (mol)				
1	3.6×10^{-5}	94.3	2.54×10^5	1.495	[Gelx] = 1 g
2	7.3×10^{-5}	104.5	2.75×10^5	1.531	[MMA] = 0.047 mol
3	1.1×10^{-4}	192.9	4.16×10^5	1.865	[Water] = 20 mL
4	1.47×10^{-4}	233.6	5.41×10^5	1.739	[Temp] = 70°C
5	1.84×10^{-4}	264.6	4.39×10^5	2.424	
			Effect of Dilution		
	Water (mL)				
1	10	383.2	4.17×10^5	3.702	[Gelx] = 1 g
2	25	264.8	4.08×10^5	2.61	[MMA] = 0.047 mol
3	40	161.1	3.64×10^5	1.78	[KPS] = 1.84×10^{-4} mol
4	50	149.3	1.80×10^5	3.34	[Temp] = 70°C
			Effect of Reaction Time		
	Time (min)				
1	30	119.2	3.55×10^5	1.36	[Gelx] = 1 g
2	45	107.2	1.56×10^5	2.75	[MMA] = 0.047 mol
3	60	170.6	6.44×10^5	1.07	[KPS] = 1.84×10^{-4} mol
4	90	351.7	7.53×10^5	1.882	[Water] = 20 mL
					[Temp] = 70°C

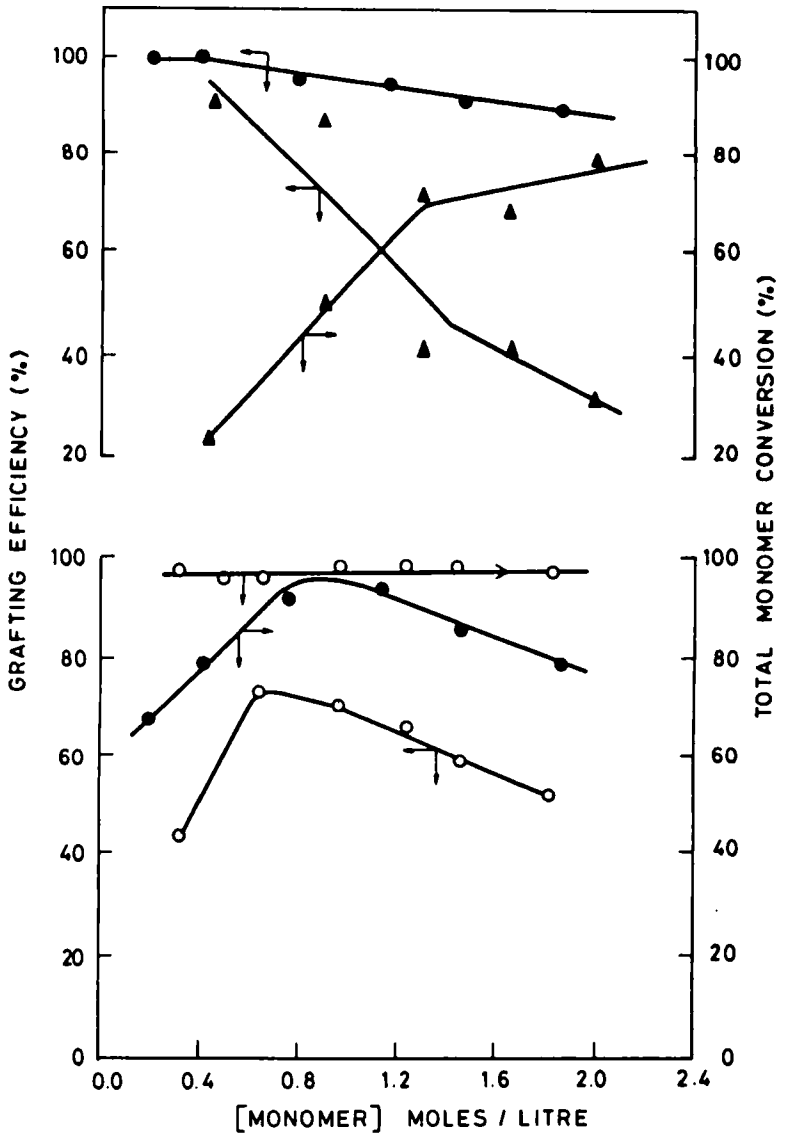

FIG. 5. Total percentage conversion of the monomer and grafting efficiency as a function of monomer concentration. (●) MMA, (○) AA, and (▲) VAc. Experimental details as given in Fig. 2.

The Initiation, Propagation, and Termination

The results presented in Tables 2 and 3 and Figs. 5–8 can only be discussed with these three steps taken together. With water-soluble monomers, one expects a higher frequency of grafting because the Gelx granules invade the medium containing monomer and initiator. This provides a localized environment conducive for the

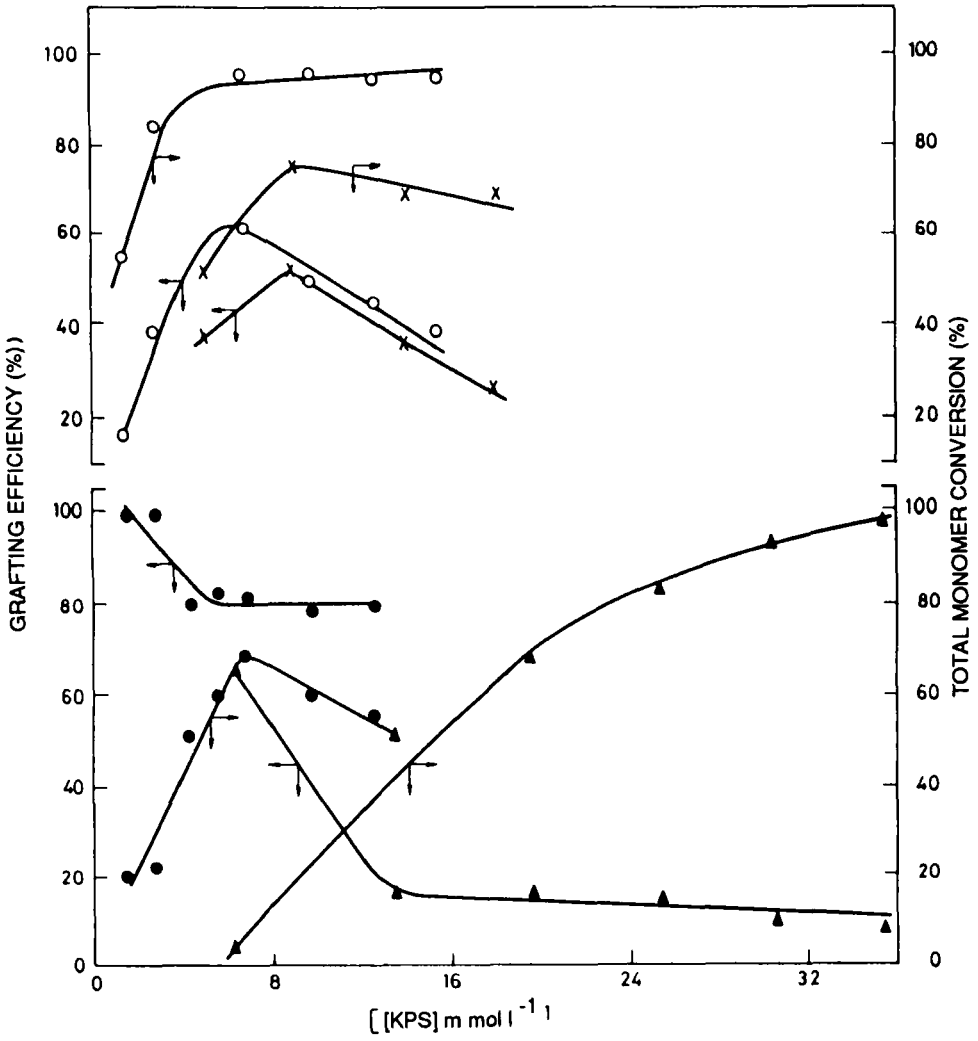

FIG. 6. Total percentage conversion and grafting efficiency as a function of initiator concentration. (●) MMA, (○) AA, (▲) VAc and (×) Aam. Experimental details as given in Fig. 3.

initiation and propagation of grafting. In general, this situation vaguely resembles suspension polymerization. These microdomains of high activity within the swollen granules lead to unusually high percentages of grafting characteristic of heterophase polymerizations [11]. With methyl methacrylate the frequency of grafting is low but the molecular weights are high. This could very well be due to the insolubility of the monomer in water. However, a very interesting consequence occurs here. The grafted chains preferentially absorb the monomer from the medium. This situation is highly favorable for a smooth propagation step, leading to high molecular weight grafts [10].

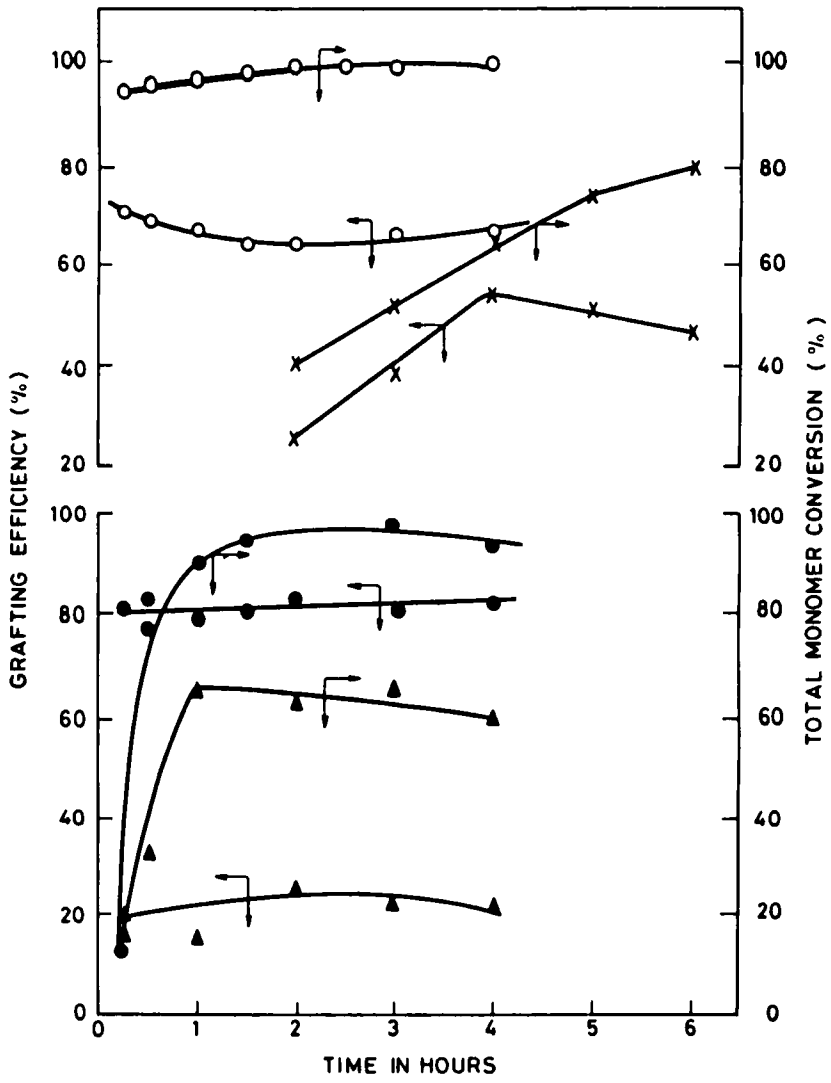

FIG. 7. Total percentage conversion of the monomer and grafting efficiency as a function of time. (●) MMA, (○) AA, (▲) VAc and (×) Aam. Experimental details as given in Fig. 4.

The degree of polymerization $\overline{X}_n$ is equally dependent on all the termination steps and the propagation step because

$$\overline{X}_n = \frac{\text{rate of growth}}{\Sigma \text{ rate of all reactions leading to a dead polymer}}$$

While the swellability of PAA grafts and the water solubility of the monomer and initiator facilitate chain termination as much as does chain propagation, the former event will be delayed in the Gelx-*g*-PMMA system due to the preferential absorption of the monomer alone. An equally important factor is the chain transfer

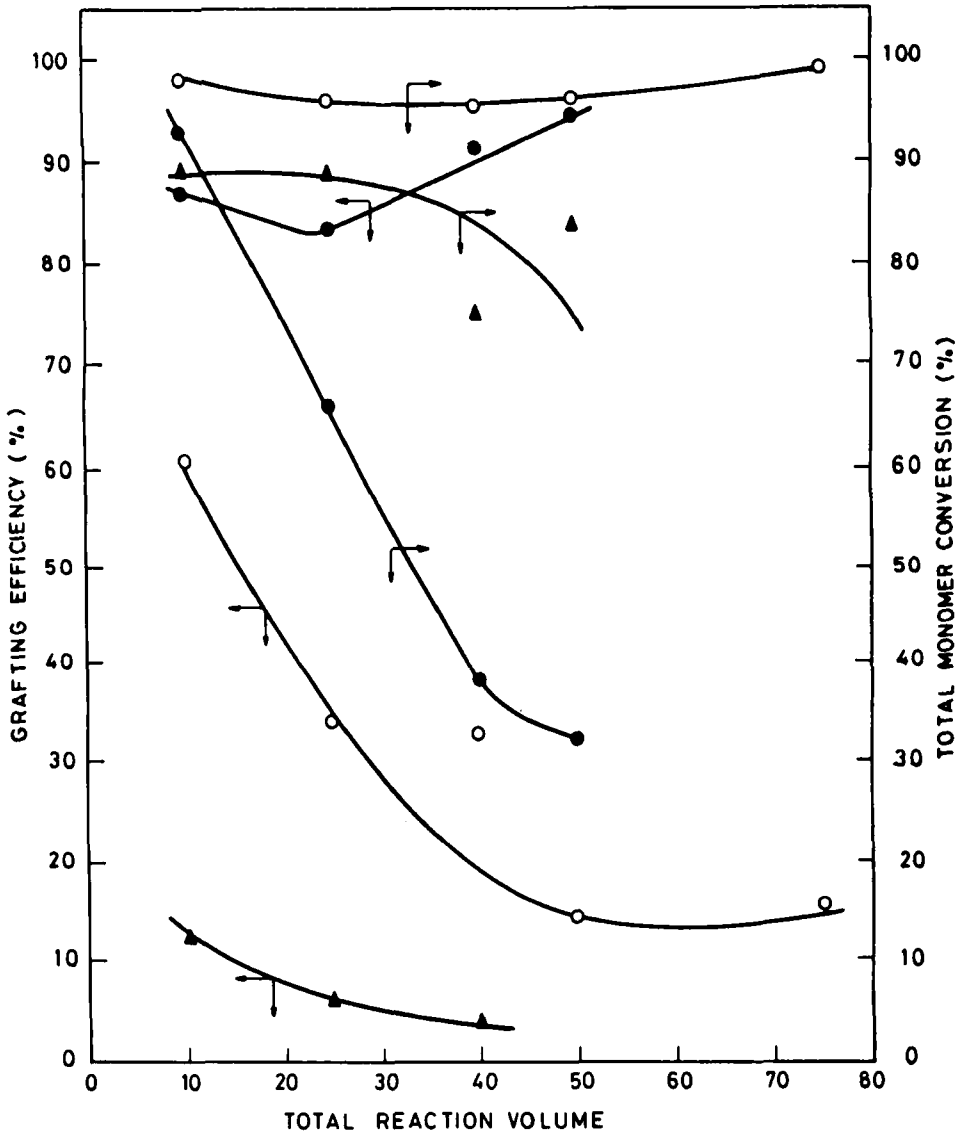

FIG. 8. Total percentage conversion of the monomer and grafting efficiency as a function of total reaction volume. (●) MMA, (○) AA, and (▲) VAc. Experimental details as given in Fig. 4. Time: 2 h.

characteristics of the various monomers involved. We find a close kinship between the C_M values and the grafting efficiencies. Vinyl acetate, which has C_M values 10 times larger than those of the acrylic monomers [6] considered in this work, shows the lowest grafting efficiency, whereas the acrylic monomers with comparatively lower C_M values exhibit much higher grafting efficiencies.

The validity of this line of argument is strikingly obvious from the average molecular weights of the grafts and the frequencies of grafting for Gelx-*g*-PAA and Gelx-g-PMMA listed in Tables 2 and 3, respectively.

CONCLUSIONS

Grafting copolymerizations onto insoluble matrices are influenced by the following factors:

1. Swellability of the matrix in the reaction medium
2. Solubility of the monomer/initiator in the reaction medium
3. Preferential absorption of the monomer/initiator by the grafted chains

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