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HYDROPHILIC CROSSLINKED GELATIN CORE WITH HYDROPHOBIC POLYMETHYL ACRYLATE GRAFTS. CONDITIONS OF GRAFTING AND CHARACTERISTICS OF THE GRAFT COPOLYMER†

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ABSTRACT

A simple treatment of gelatin granules with aqueous glutaraldehyde (GLA) yields a versatile crosslinked matrix. The crosslinking involves the ϵ-amino groups of the lysine residues of the protein and the aldehyde functionality of the GLA. Grafting of this matrix with methyl acrylate results in a very interesting material which has a hydrophilic core but anchors hydrophobic grafts. Here we report the preparative details and essential characteristics of this versatile graft copolymer.

INTRODUCTION

Gelatin is the single-stranded degradation fragment of the triple-stranded structural protein collagen. In our search for materials that perform like engineering plastics yet degrade like natural polymers, we have been investigating various combinations of gelatin with synthetic polymers [1–4]. We first introduced collagenlike crosslinks in gelatin to

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reduce its water solubility and to improve its biological resistance by reacting it with glutaraldehyde. This reaction involves the ϵ-amino groups of the lysine residues and the aldehyde functionality of glutaraldehyde, but goes beyond the formation of aldimine. In solution, glutaraldehyde exists in the oligomeric state, and these species could give rise to the formation of Michael-type adducts with amines which are stable even at very low pH [5, 6]. While gelatin is soluble in water, crosslinked gelatin (Gelx) can only swell. Earlier, we reported the kinetics of grafting of this matrix with the monomer acrylamide in aqueous medium using persulfate initiator [2]. As reported there, the reactants and products were water soluble except for Gelx and (Gelx-*g*-PAam), where PAam = polyacrylamide. Thus, while the homopolymerization followed general solution kinetics, the grafting occurred under heterogenous conditions. In the present study, except for the initiator, all other ingredients are water insoluble. A detailed and systematic analysis of the effects of the monomer and initiator concentrations, time, and dilution on the percentage grafting and grafting efficiency are essential to arrive at optimum reaction conditions. We present here the results of such an investigation. We specifically chose methyl acrylate because subsequent partial hydrolysis of the ester moiety could improve the total hydrophilic properties of the material.

EXPERIMENTAL

Bacteriological gelatin, methyl acrylate, and glutaraldehyde (25% aqueous solution) were supplied by Loba Chemicals, Bombay. Potassium persulfate and A.R. grade solvents were used as such. All reactions were carried out in oxygen-free distilled water.

The following abbreviations have been used in the text:

Gelatin	Gel
Crosslinked gelatin	Gelx
Methyl acrylate	MA
Polymethyl acrylate	PMA
Potassium persulfate	KPS
Crosslinked gelatin with polymethyl acrylate grafts	Gelx-*g*-PMA

Preparation of Gelx

Gelatin was crosslinked using aqueous glutaraldehyde as described earlier [1, 5, 6]. The crisp granules were washed thoroughly with water and later with acetone. The sample was subsequently dried under vacuum at 40°C.

Preparation of Gelx-*g*-PMA

Reaction flasks with specified quantities of Gelx, MA, KPS, and water were kept in a thermostat shaker maintained at the requisite temperature to ensure uniform conditions. To end the reaction, hydroquinone was first added to quench the reaction and then the reaction mixture was extracted exhaustively in a Soxhlet with acetone to remove the homopolymer. Soxhlet extraction was done until the residue registered constant weight. The PMA was reprecipitated with ethanol and dried under vacuum at 40°C.

The percentage grafting and grafting efficiencies were calculated as follows [7]:

$$\% \text{ grafting} = \frac{(\text{total weight of graft copolymer}) - (\text{weight of Gelx})}{\text{weight of Gelx}}$$

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

The grafts were stripped off the matrix by acid hydrolysis in 6 *N* HCl at 110°C for 24 h, and the molecular weights were determined viscometrically [8]. A Leeds & Northrup (U.S.A.) DTA Unit was used to study the thermal behavior of Gelx, Gelx-*g*-PMA, and PMA. The heating rate was maintained at 10°C/min. The IR scans were done in a Shimadzu (200) unit as KBr pellets.

RESULTS AND DISCUSSIONS

The (Gelx–persulfate–MA) graft copolymerization system is triphasic, with Gelx forming the solid phase, methyl acrylate the nonaqueous phase, and aqueous persulfate the continuous phase. Homopolymerization can occur at the liquid/liquid (aqueous/monomer) interphase, while graft copolymerization involves all three phases.

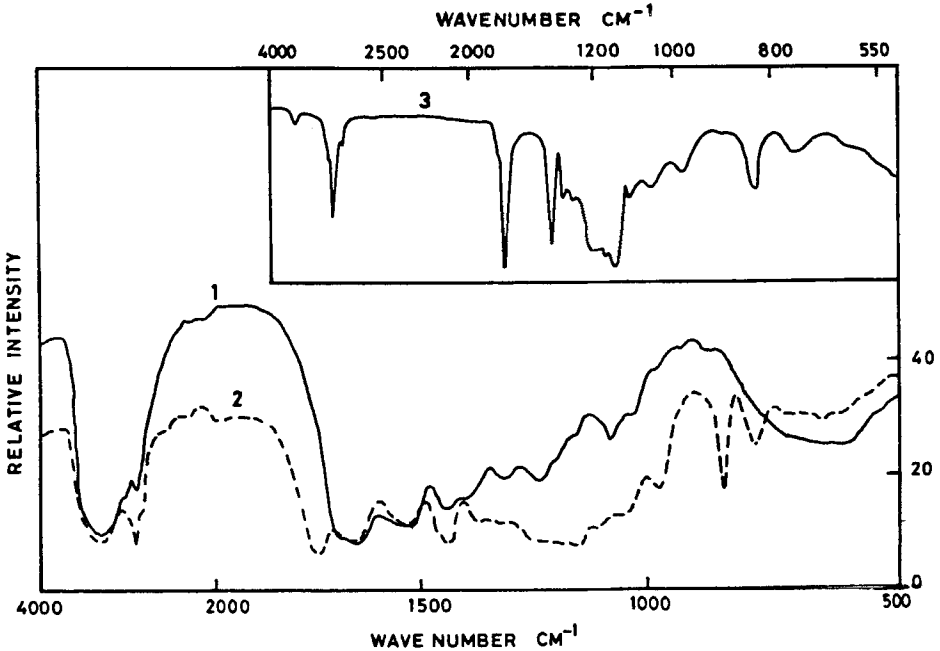

FIG. 1. IR spectra of (1) Gelx, (2) Gelx-g-PMA, and (3) PMA. For details, see text.

Gelx and Gelx-*g*-PMA show an absorption band at 1640 cm^{-1} due to amide linkages and aldimine linkage. Absorption due to N—H stretching appears at 3200–3500 cm^{-1} and N—H deformation at 1540 cm^{-1}. Absorption bands at 2920 and 1440 cm^{-1} are due to C—H stretching and deformation, respectively. Absorption at 1740 cm^{-1} is due to carbonyl absorption of the ester moiety.

The presence of 1740 cm^{-1} absorption in Gelx-*g*-PMA together with strong 2920 and 1440 cm^{-1} absorptions (C—H stretching and deformation, respectively), indicate that grafting has taken place (Fig. 1).

The dependence of percentage grafting, grafting efficiency, and total percentage conversion on time are given in Fig. 2. Induction periods of short duration are observed. It is possible that the creation of radical centers on the Gelx is the rate-determining step; however, once the initiation sites are formed, the grafting competes with homopolymerization.

The influence of initiator and monomer concentrations on percent-

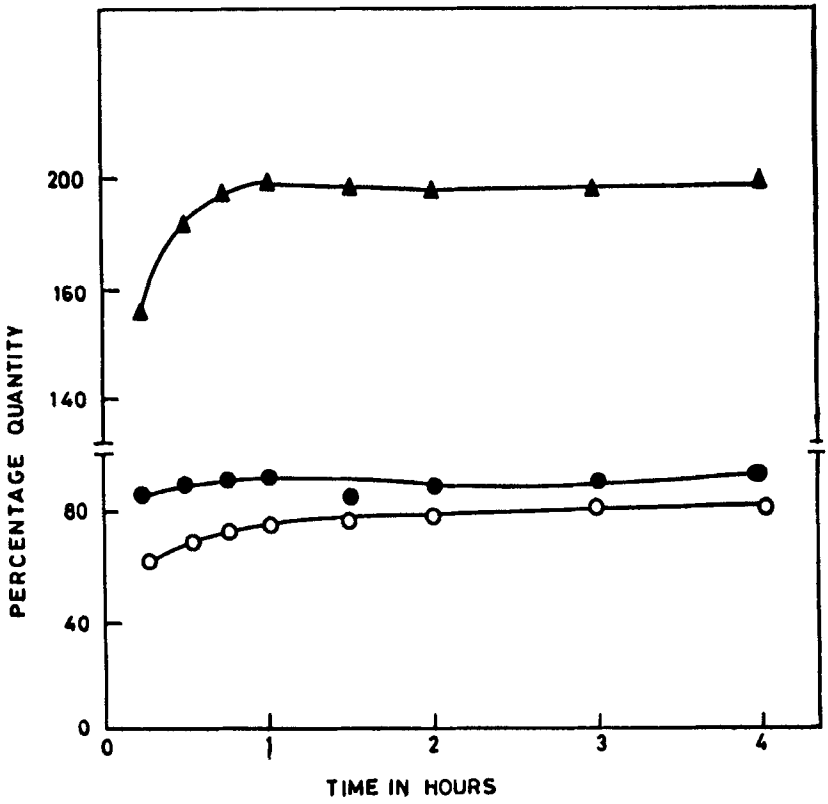

FIG. 2. Effect of time on percentage grafting (▲), percentage conversion (○), and grafting efficiency (●). Gelx = 1 g, MA = 1.667 mol/L, KPS = 13.87 mmol/L, volume = 20 mL, 65°C.

ages grafting, grafting efficiency, and total percentage conversion are depicted in Figs. 3, 4, and 5. The percentage grafting and grafting efficiency reach saturation at higher concentrations of the initiator. However, the grafting efficiency decreases with increasing monomer concentrations, indicating that homopolymerization becomes more efficient at higher monomer concentrations.

In heterophase reactions the surface and swelling characteristics of the insoluble component in the reaction medium become the focal points. When we consider grafting an insoluble, yet swellable matrix, like Gelx, the extent to which the matrix can imbibe the monomer and

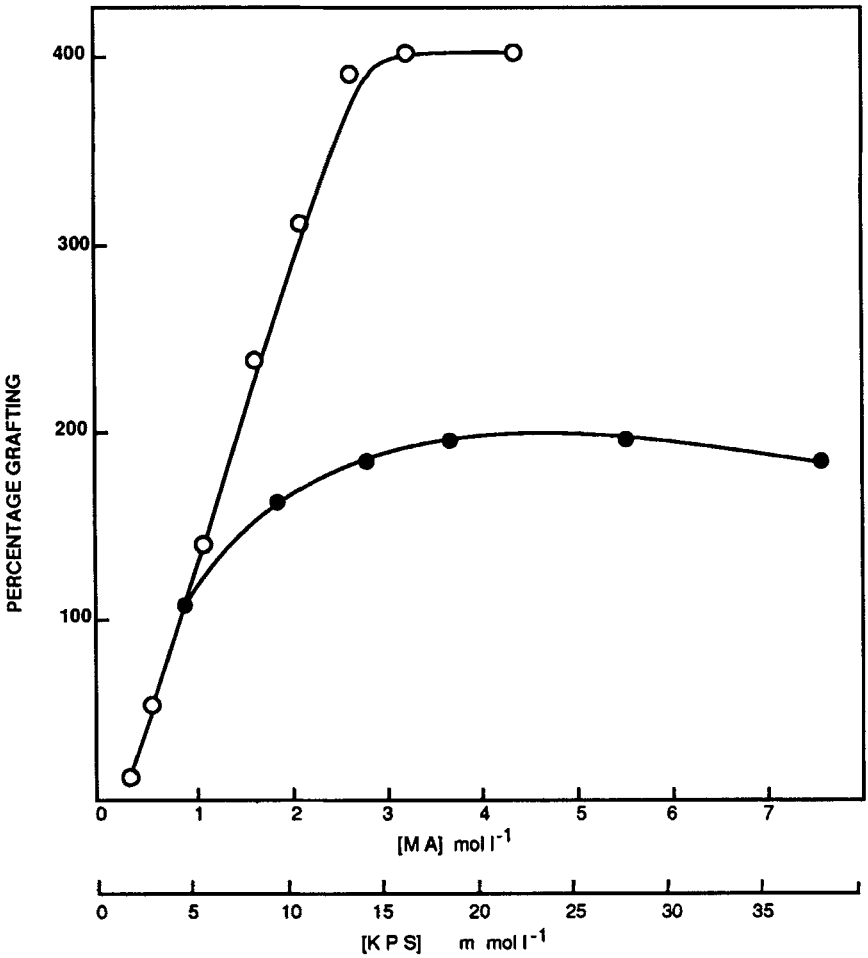

FIG. 3. Effect of initiator (●) and monomer (○) concentrations on percentage grafting. Gelx = 1 g, KPS = 13.87 mmol/L, MA = 1.667 mol/L, volume = 20 mL, time = 2 h, 65°C.

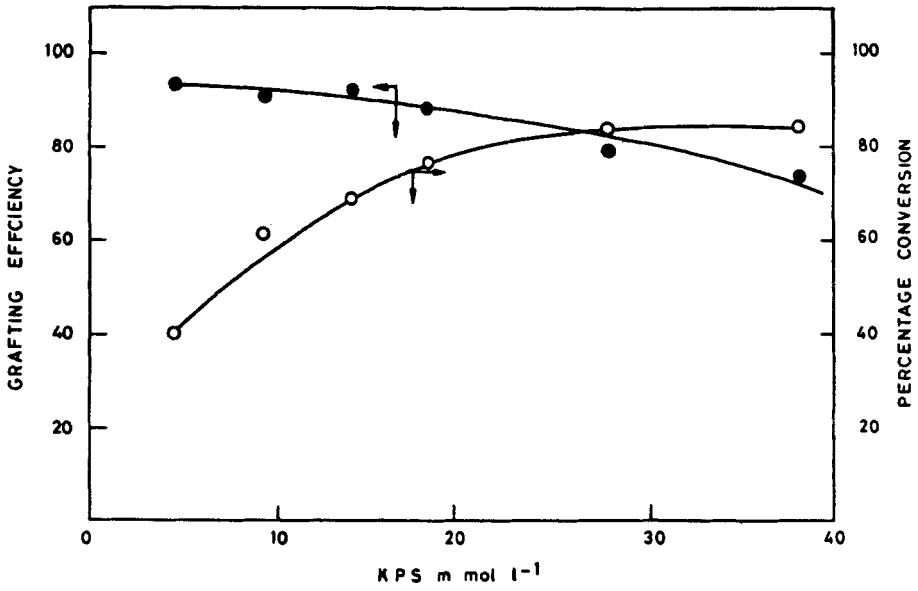

FIG. 4. Effect of KPS concentration on grafting efficiency (●) and percentage conversion (○). Gelx = 1 g, MA = 1.667 mol/L, volume = 20 mL, time = 2 h, 65°C.

initiator are important factors, since this determines the course of initiation, propagation, and termination reactions. The propagation and termination steps will proceed with equal probability if the grafted matrix can absorb the monomer and initiator fragments with the same frequency. However, if there is preferential uptake of the monomer, then the propagation will proceed unhindered, yielding unusually long grafted chains. When we investigated the persulfate-initiated grafting of Gelx with acrylamide in an aqueous medium earlier, we observed that high concentrations of the initiator and monomer suppressed the swellability of the Gelx granules [2]. However, in the present case, the monomer, methyl acrylate, is not water soluble, and we found that its uptake by the granules is practically nil. This preferential absorption of the initiator, together with the hydrophobic nature of the growing chain, results in high molecular weight grafts.

Earlier reports [9, 10] suggested that in persulfate-initiated graft copolymerizations of gelatin with vinyl monomers, free radical centers are

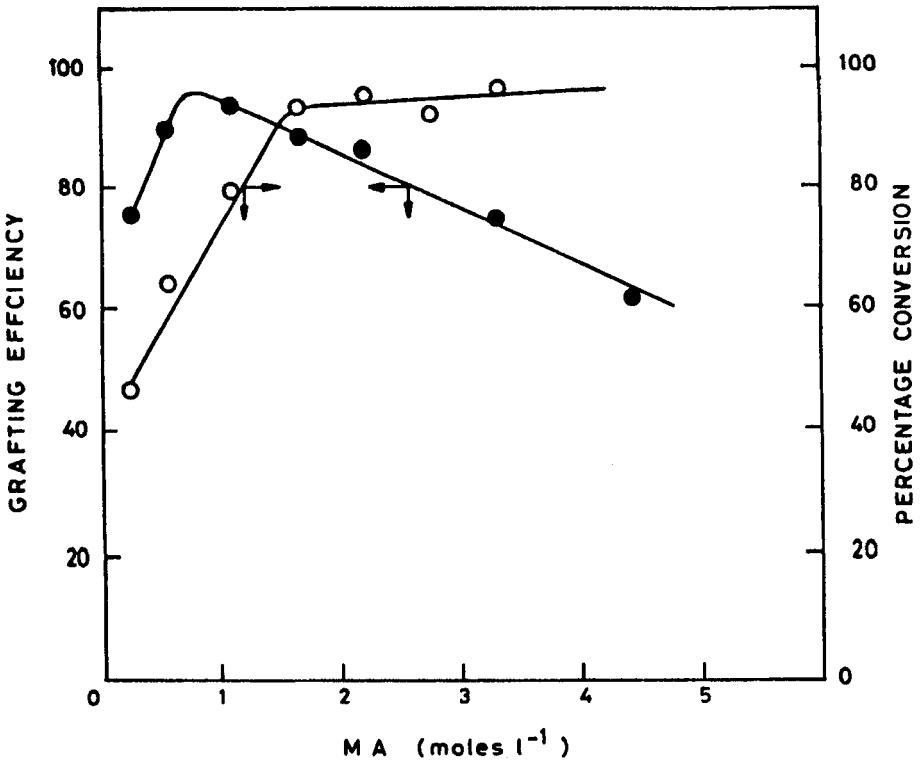

FIG. 5. Effect of monomer concentration on grafting efficiency (●) and percentage conversion (○). Gelx = 1 g, KPS = 13.87 mmol/L, volume = 20 mL, time = 2 h, 65°C.

created on the protein chain through hydrogen abstraction. Once the initiation centers are formed, the chain propagation and termination follow normal heterogeneous kinetics.

$$S_2O_8^{2-} \xrightarrow{\text{decomposition}} 2SO_4^{\bullet -}$$

$$\text{Gelx} + R^{\bullet} \xrightarrow{\text{H abstraction}} R{-}H + {}^{\bullet}\text{Gelx}$$

We compared the amino acid analysis data of Gelx and Gelx-PMA to identify the grafting sites. The results show the sites to be randomly

distributed with no preference for hydrogen abstraction from any particular residue.

Table 1 lists the average molecular weight profiles of the grafted chains and an estimate of the number of grafting sites per mole of gelatin. While average molecular weight registers a decrease with an increase in initiator concentration, the number of grafting sites increases. With an increase in monomer concentration, both the molecular weights of the grafts and the number of grafting sites show a definite increment. The influence of time and dilution on these quantities is marginal. These observations are consistent with general free radical polymerization kinetics [11].

The thermal behaviors of Gelx, Gelx-*g*-PMA, and PMA are presented in Fig. 6. The high temperature exothermic peaks appear as a result of the decomposition of the polymers. The endothermic peaks may be due to phase transition. Low temperature peaks ($<150°C$) may be due to loss of moisture since they disappear on preheated samples [12].

Physical observation of melting point measurements of Gelx and Gelx-*g*-PMA shows a sudden change (softening) above 300°C. Gelx thermogram also shows this. There is no change in Gelx-*g*-PMA up to 340°C, suggesting slightly improved thermal stability.

CONCLUSIONS

Crosslinked gelatin was graft copolymerized with methyl acrylate under heterophasic condition. Short induction periods were observed, suggesting the possibility that the creation of radical centers on the Gelx could be the rate-determining step. It was observed that while the average molecular weight of the grafts and the frequency of grafting increased with an increase in monomer concentration, increasing the initiator concentration led to a decrease in average molecular weight and an increase in grafting frequency.

TABLE 1

No.	Percentage of grafting	Molecular weight	Number of grafting sites per mole of gelatin	Conditions of grafting
				Gelx = 1 g; monomer = 1.667 mol/L; water = 20 mL; 65°C; time = 2 h
1	108.1	9.72×10^4	4.49	KPS = 4.63 mmol/L
2	161.7	7.65×10^4	8.53	" 9.24 "
3	182.7	6.57×10^4	11.23	" 13.87 "
4	195.1	6.28×10^4	12.55	" 18.44 "
5	191.0	5.30×10^4	14.56	" 27.74 "
6	179.3	5.11×10^4	13.81	" 36.99 "
				Gelx = 1 g; KPS = 13.87 mmol/L; water = 20 mL; 65°C; time = 2 h
1	23.6	1.47×10^4	5.48	Monomer = 0.277 mol/L
2	58.1	3.31×10^4	7.09	" 0.555 "
3	111.9	4.70×10^4	9.61	" 1.110 "
4	185.8	5.28×10^4	14.21	" 1.665 "
5	263.2	8.06×10^4	13.19	" 2.220 "
6	310.6	9.08×10^4	13.81	" 2.776 "

				Gelx = 1 g; KPS = 13.87 mmol/L; monomer = 1.667 mol/L; 65°C; water = 20 mL
1	156.3	4.67×10^4	13.52	Time 15 min
2	185.4	2.77×10^4	27.04	" 30 "
3	193.6	5.41×10^4	14.45	" 45 "
4	198.7	6.21×10^4	12.90	" 60 "
5	197.1	3.86×10^4	20.62	" 90 "
6	196.4	3.68×10^4	21.56	" 180 "
				Gelx = 1 g; KPS = 13.87 mmol/L; monomer = 1.667 mol/L; 65°C; time = 2 h
1	189.6	8.57×10^4	8.93	Water 10 mL
2	102.9	4.53×10^4	9.17	" 25 "
3	78.2	5.44×10^4	5.8	" 40 "
4	110.4	4.19×10^4	10.64	" 50 "
5	136.6	4.48×10^4	12.37	" 75 "

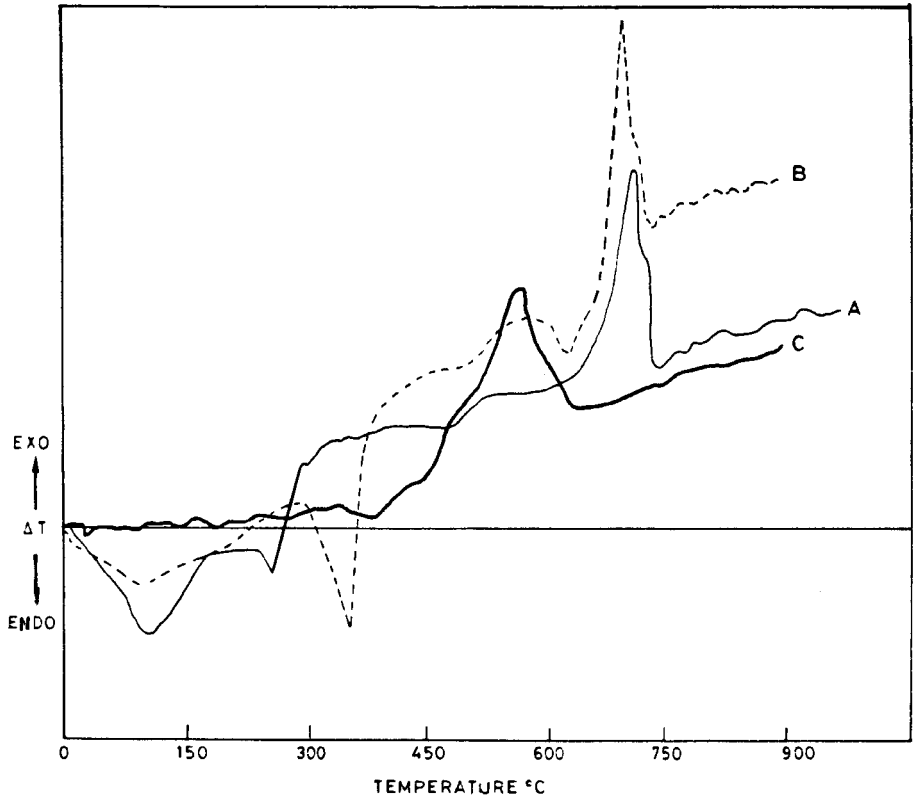

FIG. 6. Thermal behavior of (A) Gelx, (B) Gelx-*g*-PMA, and (C) PMA.

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