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SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS OF ACRYLIC ACID ONTO POLY VINYL CHLORIDE USING DI-(2-PHENOXY ETHYL) PEROXY DICARBONATE INITIATOR

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SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS OF ACRYLIC ACID ONTO POLY VINYL CHLORIDE USING DI-(2-PHENOXY ETHYL) PEROXY DICARBONATE INITIATOR

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ABSTRACT

Graft copolymerization of acrylic acid onto Poly vinyl chloride (PVC) was carried out in nitrobenzene using di-(2-phenoxy ethyl) peroxy dicarbonate as an initiator. The effect of various parameters such as initiator, monomer concentrations, reaction temperature and time on percent grafting was examined. The graft copolymers were characterized by Viscosity, Infrared Spectroscopy (IR) and Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC). The thermal stability of graft copolymers increased whereas intrinsic viscosity decreased as percent grafting was increased. Maximum grafting of 3.0% was obtained. The activation energy and collision frequency factor for graft copolymerization was found to be 4.54 Kcal/mol and 0.8788×10^2, respectively.

Key Words: Poly vinyl chloride; Acrylic acid; Grafting, Di-(2-Phenoxy ethyl) peroxy dicarbonate; Intrinsic viscosity.

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INTRODUCTION

The graft copolymerization of vinyl monomers on to PVC has been extensively reviewed by R. J. Ceresa [1]. PVC can be modified by grafting acrylic monomers imparting ion exchange [2], fogging inhibition [3] properties and improving thermal stability and processability [4]. The grafting can be achieved by radiation or free radical polymerization. In radiation grafting technique, the sources used are γ-radiation [5-8], low temperature plasma radiation [9-10], argon glow discharge [11] and UV radiation [12]. Many researchers have attempted and achieved high monomer grafting efficiency as high as >100% through heterogeneous radiation technique [13-16]. In other methods, the grafting of monomer is carried out onto PVC, modified through thiolation [17], hydroboration [18] and xanthate macro initiator [19]. Many people have used the dehydrochlorinated PVC to improve the grafting ratio [20-22]. Gupta *et al*. [12] grafted silane monomer onto PVC keeping the conditions for minimum dehydrochlorination. Wulff *et al*. [23] used the diisopropyl peroxydicarbonate initiator to graft butyl acrylate and butadiene onto PVC. The grafting of acrylic acid onto PVC in nitrobenzene using di-(2-phenoxy ethyl) peroxy dicarbonate is not been attempted so far. In the present paper, an attempt has been made to introduce carboxylic functionality onto PVC by grafting acrylic acid with minimum dehydrochlorination using a novel initiator di-(2-phenoxy ethyl) peroxy dicarbonate and nitrobenzene as solvent (polymerization medium). It was determined that nitrobenzene which is a retarder (not a inhibitor) should give a low graft level of monomer. The kinetics of graft copolymerization, intrinsic viscosity and thermal properties were also investigated.

EXPERIMENTAL

Materials

Poly vinyl chloride, Indovin, (67EF092) (K-value 67 in 1% cyclohexanone) and inherent viscosity 0.92, was obtained from M/s. IPCL, Vadodara, India. It was purified by washing with acetone to remove physical impurities, filtered, and dried in vacuum at room temperature. Acrylic acid (Fluka - Germany) was purified by vacuum distillation. Di-(2-phenoxy ethyl) peroxy dicarbonate [Percidol] (M/s. Peroxide India Ltd., Madras, India) was recrystallized from acetone. Nitrobenzene, methanol, THF and acetone (AR grade, M/s. Ranbaxy Laboratories, India) were used as received.

Synthesis

The graft copolymerization was carried out in a two necked round bottom flask, equipped with a condenser, nitrogen inlet, magnetic stirrer and kept in a thermostatically controlled oil bath. A known amount of PVC was dissolved at room temperature in nitrobenzene to a clear, transparent solution and then required amount of initiator and acrylic acid was added to above solution. The reaction was carried out under nitrogen atmosphere for 3.0 hours at 70°C. The reaction mixture was cooled to room temperature rapidly and reprecipitated with methanol. The polymer obtained was filtered and washed throughly with methanol to remove unreacted and homopolymer of acrylic acid. This purified polymer was dried under vacuum at 40°C and soxhlet extracted with methanol for 24 hours to remove homopolymer of acrylic acid and finally dried under vacuum at 40°C to a constant weight.

Percent Grafting

The percent grafting of acrylic acid onto PVC and percent conversion of monomer to graft copolymer was determined by non-aqueous titration method using the following equations:

$$\text{Acid number of graft copolymer (AN)} = \frac{V_2\text{-}V_1 \text{ X } N_{KOH} \text{ X } 56.1}{W}$$

$$\text{Acrylic acid grafted (\%) (Aag)} = \frac{\text{AN X MW}}{56.1 \text{ X F}}$$

where V_2 = volume of KOH consumed by graft copolymer (ml), V_1 = volume of KOH consumed by standard PVC (ml), N_{KOH} = normality of methanolic KOH solution, MW = molecular weight of acrylic acid, F = functionality of acrylic acid, and W = weight of graft copolymer (gm).

$$\text{Weight of monomer grafted (gms) (Wmg)} = \frac{\text{Aag X } W_{PVC}}{100}$$

$$\text{Conversion of monomer to graft copolymer (\%)} = \frac{\text{Wmg X 100}}{\text{Wmc}}$$

where W_{PVC} = weight of original PVC taken (gm), Wmg = weight of monomer grafted (gm), Wmc = weight of monomer charged (gm).

A blank experiment was also carried out under identical conditions without addition of acrylic acid to prepare a standard PVC sample. A blank titration was also carried out for standard PVC sample in THF.

Characterization

Infrared Spectroscopy

The films of PVC graft copolymers were prepared by dissolving them in THF (2% w/w) and casting on a glass plate. The films were dried under vacuum at room temperature for 24 hours. The IR spectra of the films were recorded on a Shimadzu I.R. Spectrophotometer from 400-3600 cm^{-1}.

Viscosity Measurements

Intrinsic viscosity (dL/g) of soxhlet extracted samples (0.5% w/w, THF) were measured using a Ubbelohde Capillary Viscometer (AVS 400 SCHOTT-GERATE, Germany) at 30 ± 1°C.

Thermal Analysis

DSC/TGA thermogravimetric traces were recorded on a Dupont-DSC-910 thermal analyzer with a heating rate of 10°C/min under nitrogen atmosphere from 25°C to 300°C and 450°C, respectively. The initial decomposition temperature (IDT), integral procedural decomposition temperature (IPDT) and the temperature at which sample undergoes 50% decomposition (T_{50}) were calculated. The apparent activation energy for thermal decomposition (EaT) of the virgin and graft copolymers were also determined.

RESULTS AND DISCUSSIONS

The effect of various reaction parameters viz. monomer and initiator concentration, temperature and time, on percent grafting was studied and the results are discussed below:

Effect of Initiator Concentration on Grafting

The effect of variation of initiator concentration from 0.05 to 1.0 wt% at 60°C and 70°C on percent grafting was studied and the results are given in Figure 1. The conversion of monomer to graft copolymer with the change in initiator concentration is given in Table 1. When the grafting experiments were carried out at 60°C, it was observed that as initiator concentration increases up to 0.5%, the percent grafting also increases and then levels off. Similarly, at 70°C, the percent grafting increases up to 0.5% of initiator concentration, but then further it decreases. The increase in percent grafting with increase in initiator concentration

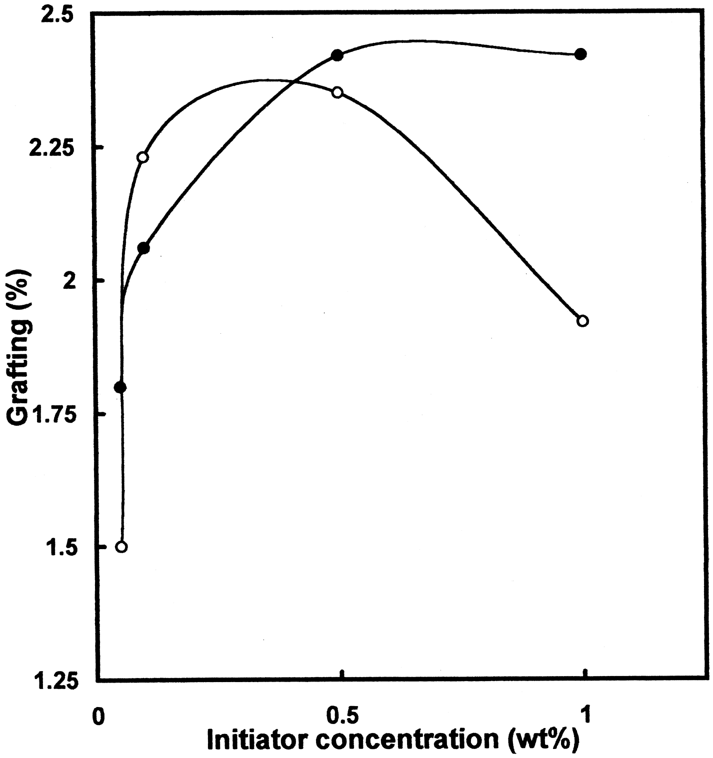

Figure 1. Effect of initiator concentration on grafting. (o) 60°C, (·) 70°C, PVC: 5.0 g, Acrylic acid: 0.5 g, Reaction time: 3 hours.

Table 1. Effect of Various Reaction Parameters on Conversion

Temp. (°C)	Initiator		Monomer		Time		Temp. (°C)	Conversion (%)
	%	Conv.(%)	%	Conv.(%)	h	Conv.(%)		
60	0.05	18.0	5	21.6	1	20.8	55	22.0
	0.10	20.6	10	24.2	3	24.2	60	24.2
	0.50	24.2	15	14.9	5	30.4	62.5	25.2
	1.00	24.2	20	10.8	7	30.0	65	26.2
							70	19.2
							75	15.4
70	0.05	15.0	5	32.4	1	12.8		
	0.10	22.2	10	19.2	3	19.2		
	0.50	23.4	15	16.3	5	29.4		
	1.00	19.2	20	11.8	7	27.2		

is due to availability of more number of free radicals. At higher initiator concentration the number of free radicals decreases due to recombination of free radicals.

Acrylic acid is very sensitive to thermal polymerization and hence, at higher temperture homopolymerization of acrylic acid is favored over graft copolymerization. This is accordance with results obtained for other such studies [22].

Effect of Monomer Concentration on Grafting

The monomer concentration was varied from 5.0 to 20 wt% at 60°C and 70°C and the results are given in Figure 2 and Table 1.

In the experiments carried out at 60°C the percent grafting increases with increase in monomer concentration up to 10% and then it decreases. Similarly, at 70°C the percent grafting increases with increase in monomer concentration up to 15% and then decreases. This is due to an increase in homopolymer (polyacrylic acid) formation rather than the graft copolymer (PVC-g-PAA). Similar results of a decrease in percent grafting with an increase in monomer concentration was

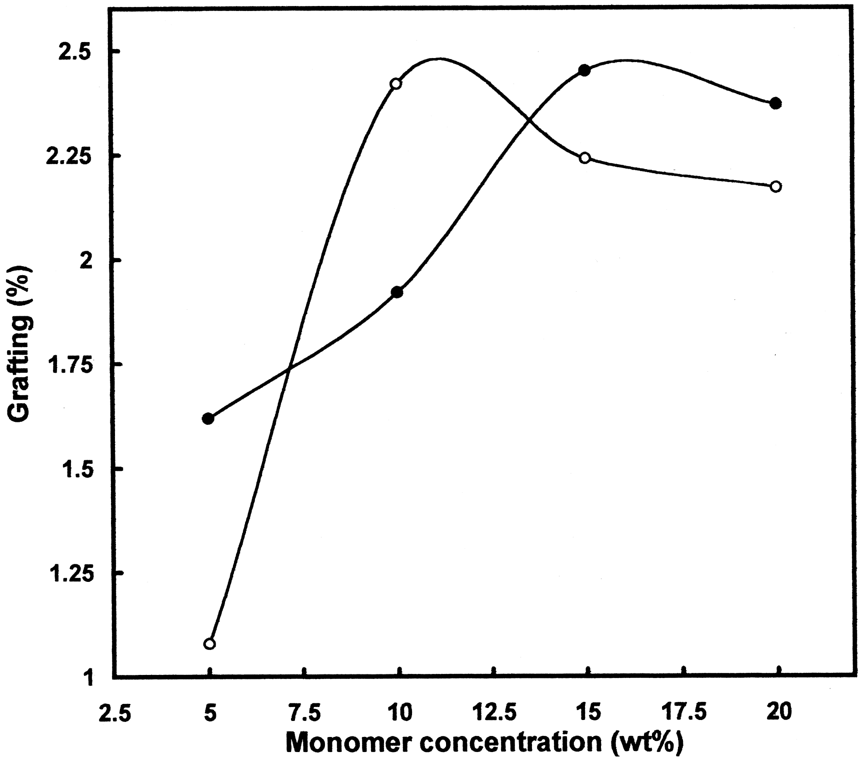

Figure 2. Effect of monomer concentration on grafting. (o) 60°C, (·) 70°C, PVC: 5.0 g, Initiator: 0.05 g, Reaction time: 3 hours.

observed by Gouloubandi and Chapiro [13] when acrylic acid was grafted onto PVC film.

Effect of Reaction Temperature on Grafting

The percent grafting increases with an increase in the reaction temperature and reaches a maximum (2.63%) up to 65°C and then decreases (Figure 3). The conversion of monomer to graft copolymer with an increase in temperature is shown in Table 1. The increase in temperature results in the formation of more free radicals, and increases the reaction rate. At a higher temperature, the free radical initiator decomposes rapidly to generate more numbers of free radicals, and at the same time thermal polymerization of acrylic acid also takes place, both of which result in an increase in the rate of homo polymerization than graft copolymerization. The initial increase and then decrease in percent grafting at a higher temperature can also be explained as follows:

It is well known that the percent grafting depends on both, the number of graft and the graft length. At a lower temperature range (50-60°C), the increase in

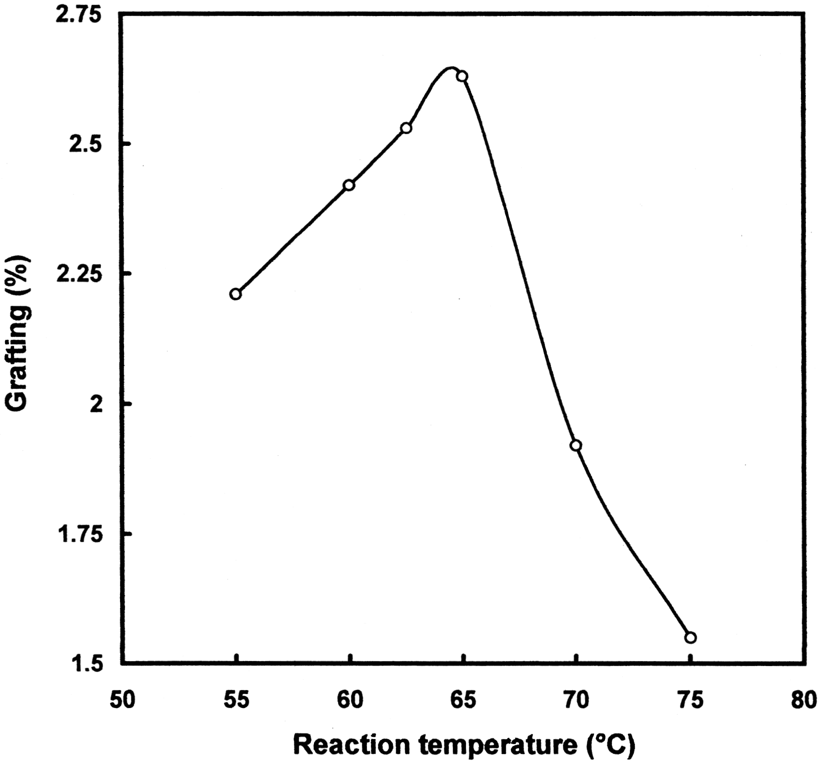

Figure 3. Effect of reaction temperature on grafting. PVC: 5.0 g, Acrylic acid: 0.5 g, Initiator: 0.05 g, Reaction time: 3 hours.

temperature increases the rate of grafting reaction and produces a large amount of grafts of longer chain lengths. But at a higher temperature range, the faster chain termination leads to short graft length and therefore, decreases the percent grafting.

Effect of Reaction Time on Grafting

The effect of reaction time on percent grafting and conversion was studied at two temperatures viz. 60°C and 70°C, and the results are given in Figure 4 and Table 1. The percent grafting increases with an increase in reaction time and reaches a maximum in 5.0 hours at 60°C and decreases with an increase in time at 70°C. The decrease in percent grafting with an increase in time beyond 5 hours may be due to mutual annihilation of grafted polymeric chains [24]. The backbone loses the grafted chains and longer grafted chains turn into the shorter chains, which reduces the overall concentration of polyacrylic acid onto PVC backbone, decreasing the percent grafting. Similar observations were made by other workers [22, 25].

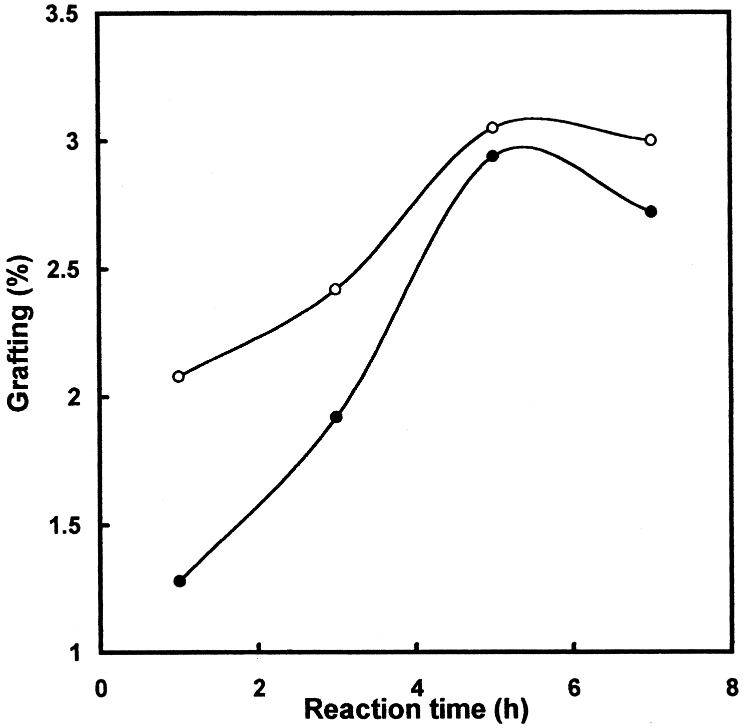

Figure 4. Effect of reaction time on grafting. (o) 60°C, (·) 70°C, PVC: 5.0 g, Acrylic acid : 0.5 g, Initiator: 0.05 g.

The maximum percent grafting of acrylic acid (3.0%) obtained in the present studies is quite low as compared to a high percent grafting of other acrylic monomers onto PVC [14, 15, 26]. This is due to the retardation phenomena of nitrobenzene, used as a solvent which plays an important role in the grafting mechanism. Nitrobenzene acts as a retarder which reacts with growing polymer chains and free radicals leading to various termination reactions [27]. Retarders are less efficient and stop only a portion of the radicals. In such cases, polymerization occurs but at a slower rate [28].

Kinetic Parameters

Apparent activation energy (Ea)

The rate constants k for graft copolymerization of acrylic acid onto PVC were calculated using the equation:

$$k= \frac{-\ln C_A}{C_{Ao}} X \frac{1}{t}$$

where C_A = final concentration of ungrafted monome, C_{Ao} = initial concentration of monomer, and t = time for grafting reaction.

From the different values of rate constants k, at different temperature T, a straight line plot of lnk against 1/T was obtained and shown in Figure 5. The apparent activation energy calculated from the slope of the straight line (Figure 5) was found to be 4.54 kcal/mol. Lee *et al*. have earlier reported the apparent activation energy as 6.1 Kcal/mol at 25-75^{o}C for heterogeneous radiation grafting of acrylic acid onto PVC fiber [29].

Apparent Collision Frequency Factor (Z)

The values of apparent collision frequency factor Z, were calculated from known values of Ea and k values at different temperature using the following equation $k= Z X e^{-Ea/RT}$ The results shows that the collision frequency is directly proportional to the temperature (Table 2).

Characterization

Infrared Spectroscopy

The IR spectra of virgin PVC; (a) and a graft copolymer containing 1.08% acrylic acid; (b) is given in Figure 6. The incorporation of polyacrylic acid (PAA) onto PVC backbone was confirmed by the appearance of a new peak in IR spec-

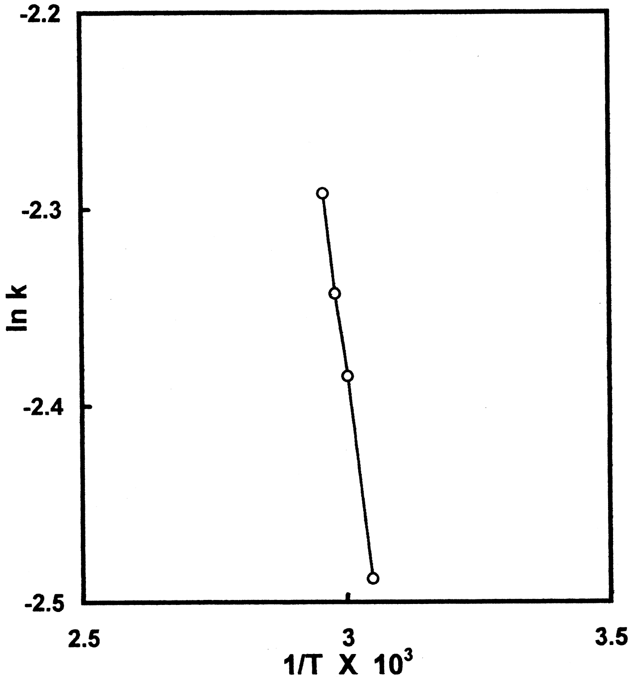

Figure 5. Measurement of apparent activation energy of graft copolymerization.

trum of soxhlet extracted graft copolymer Figure 6; (b) at 1710-1720 cm^{-1} region due to carbonyl stretching of polyacrylic acid.

Intrinsic Viscosity [η]

The intrinsic viscosity for graft copolymers decreased in comparision to virgin PVC (Table 3). As percent grafting of acrylic acid in graft copolymer increased, the viscosity decreased. The decrease in viscosity can be explained by the intense chain transfer reaction during solution grafting. In addition, the conformation of overall graft copolymer formed by the two incompatible polymer chains (PVC and PAA) might be distorted due to the grafting of PAA, resulting in

Table 2. Apparent Collision Frequency Factors for Grafting Reaction of PVC-g-PAA

(Ea) Kcal/mole	Temp. T	k	Z
4548.5	328.0	0.083	0.8820×10^2
	333.0	0.092	0.8812×10^2
	335.5	0.096	0.8735×10^2
	338.0	0.101	0.8737×10^2
Average value			0.8788×10^2

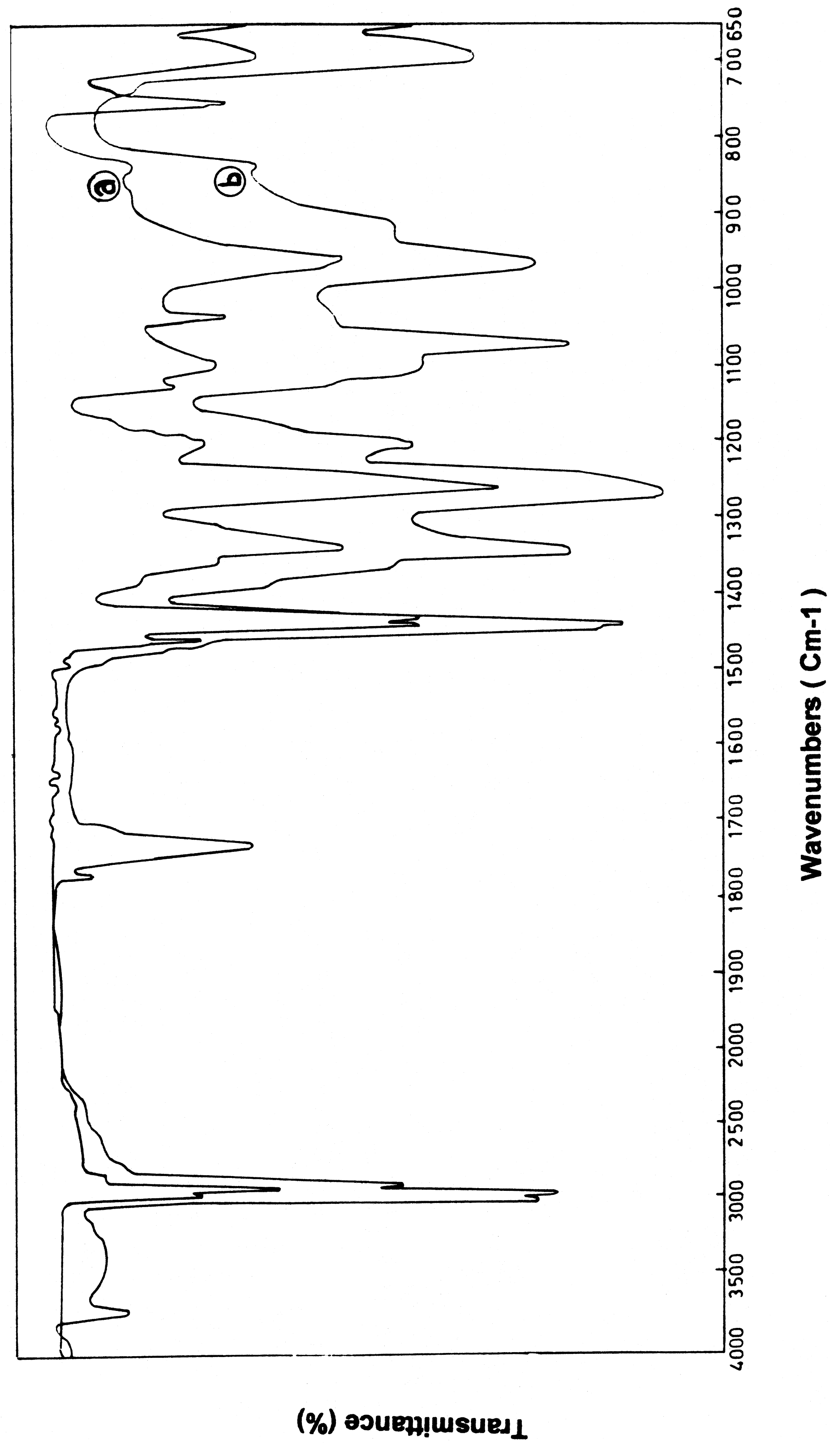

Figure 6. IR spectrum. (a) Virgin PVC, (b) PVC-g-PAA.

Table 3. Intrinsic Viscosity of Graft Copolymers

Grafting of AA (%)	Intrinsic Viscosity (dL/g)
0.00	0.891
1.08	0.867
1.62	0.857
1.23	0.836
2.94	0.821

the shrinkage of the graft which reduces the viscosity [20]. Similar results of decrease in viscosity were observed by Sathe *et al.* [25] and Gaylord *et al*. [30] for polypropylene-graft copolymers.

Differential Scanning Calorimetry (DSC)

The DSC thermogravimetric traces of virgin PVC and PVC-g-PAA copolymers are given in Figure 7. A broad endothermic shift observed in the temperature range of 50-100°C for virgin PVC represents the glass transition state of PVC [31]. The endothermic shift at 100-240°C, indicates the energy gained by polymeric chains of PVC for mobility above the glass transition state and an endothermic peak due to the complete dehydrochlorination of PVC is observed at 280°C.

In graft copolymers (PVC-g-PAA) also a shift in baseline was observed indicating the glass transition temperature (50-100°C) as found in PVC. The broad endothermic region obtained at 100-240°C and sharp endothermic peak at 280°C both shifted towards the right side on the temperature scale. The stretching of a broad and sharp endotherm for graft copolymers was due to the presence of grafted poly(acrylic acid) chains on the PVC backbone. The stretching of broad endothermic region for graft copolymers may be due to the following: (a) the grafted PAA chains gained thermal energy for the mobility; (b) anhydride formation from PAA [32]; (c) initiation of dehydrochlorination of PVC. The sharp endotherm was stretched further due to a decrease in the number of labile chlorine by grafting, which reduces the extent of dehydrochlorination of PVC.

As the percent grafting of PAA on the backbone increased, both broad and sharp endotherm stretched more towards the right side indicating the increased thermal stability of graft copolymers.

Thermogravimetric Analysis

TGA thermogravimetric traces of virgin PVC and PVC graft copolymers with different percentage graft of PAA were presented in Figure 8. The thermal decomposition of PVC occurs by dehydrochlorination at 100°C, volatilization at

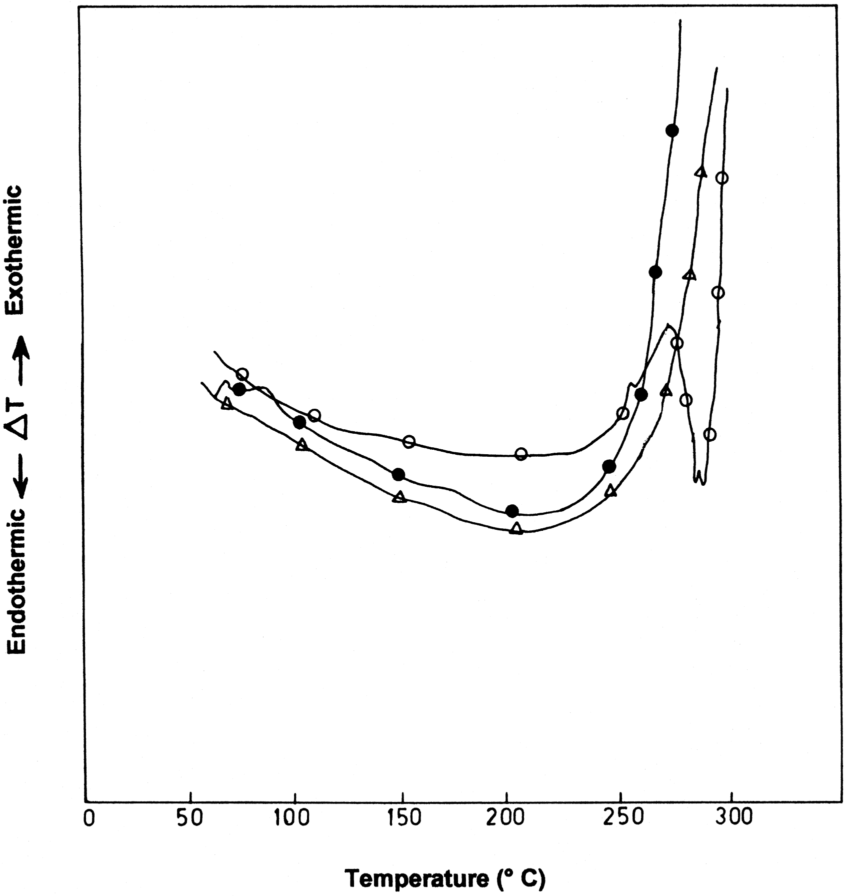

Figure 7. DSC thermograms, (o) Virgin PVC, (·) PVC-g-PAA [1.08%], and (D) PVC-g- PAA [2.94%].

200°C and, finally decomposition at 300°C. From 300°C to 380°C PVC exhibits thermal stability but again start to degrade at higher temperature (beyond 380°C). The weight loss behavior of virgin and graft copolymers are given in Table 4.

By grafting poly(acrylic acid) on to PVC backbone, the thermal stability of PVC was improved. The percent weight loss for PVC-g-PAA copolymer was less compared to virgin PVC (Table 4 and Figure 8). The IDT values for graft copolymer (205°C) are higher than virgin PVC (200°C) and it does not increase with an increase in percent grafting. The T_{50} values were increased by 5°C with 2.94% grafting (Table 5). IPDT, the indices of the thermal stability in terms of decomposition temperature was determined using Reich's method [33] in the temperature range of 25-430°C. IPDT values increased for graft copolymers. Sharma *et al.* [31] observed an increase in IPDT values up to 409°C by grafting styrene onto PVC as compared to IPDT value of 335°C for vergine PVC.

Table 4. TGA Analysis: Weight Loss of Virgin PVC and Graft Copolymers

	Weight Loss (%)		
Temp. (°C)	Virgin PVC	PVC-g-PAA[a]	PVC-g-PAA[b]
50	0.0	0.0	0.0
100	1.2	0.0	0.0
150	1.8	0.0	0.0
200	1.9	1.2	0.0
250	12.0	12.0	9.0
300	65.0	60.0	58.0
350	67.0	62.0	61.0
400	77.0	69.0	68.0
430	84.0	76.0	74.0

[a] 1.08% grafting
[b] 2.94% grafting

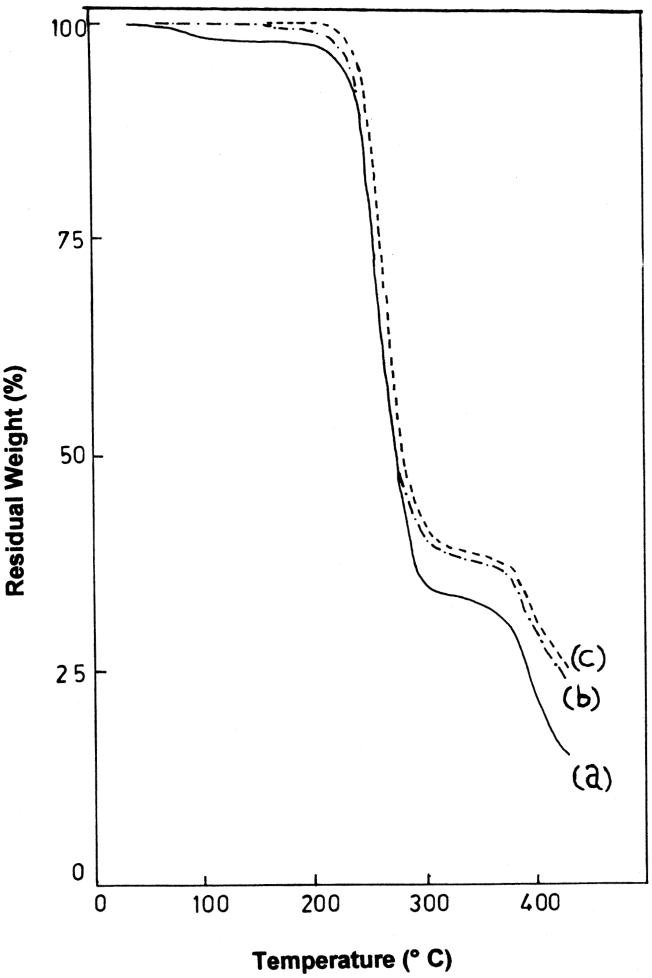

Figure 8. TGA thermograms. (a) Virgin PVC, (b) PVC-g-PAA [1.08%], and (c) PVC-g-PAA [2.94%].

Table 5. TGA Analysis of Virgin PVC and Graft Copolymers

Polymer	Graft (%)	IDT* (°C)	T_{50}* (°C)	IPDT*	EaT* Kcal/mole
Virgin PVC	0.00	200	280	305	25.2
PVC-g-PAA	1.08	205	280	316	26.5
	2.94	205	285	317	30.5

*See text.

The energy of activation for thermal degradation (EaT) for virgin PVC (Figure 9) and PVC-g-PAA (Figure 10) copolymers were determined from their TGA traces at 200-300°C region using Reich's method [34]. A plot of 1/T vs. –log ln(W_0/W) is shown in Figure 10 which gives a straight line in the regin of 200-300°C. EaT of copolymers were higher than virgin PVC. Robert Stromberg *et al.* [35] calculated the activation energy for thermal degradation of PVC and found to be 25 to 35 Kcal/mole, which depends on the type of initiator used. In the present studies, EaTs were found to be 25.2, 26.5, and 30.5 Kcal/mol for graft copolymers with 0.0%, 1.08%, and 2.94% grafting, respectively. The observed higher EaT values for graft copolymers were due to the replacement of labile chlorine which yields the low thermal stability to PVC by dehydrochlorination upon heating.

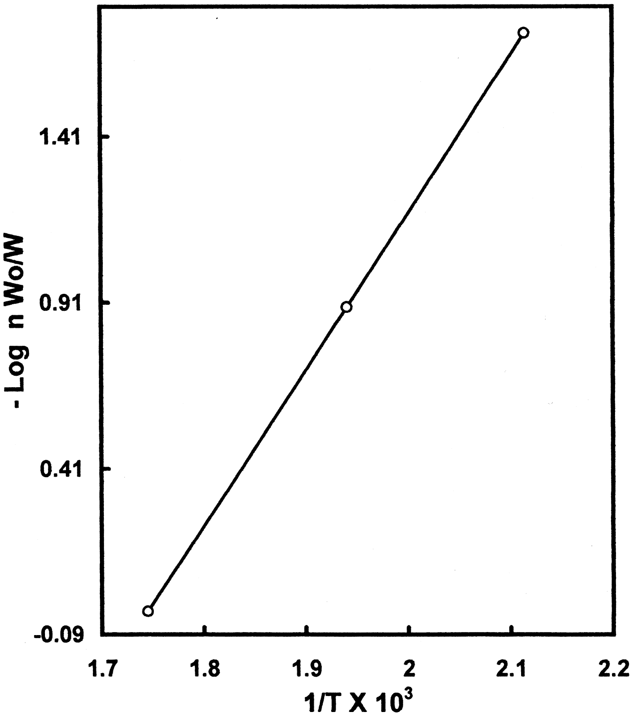

Figure 9. Determination of apparent activation energy for thermal degradation of virgin PVC.

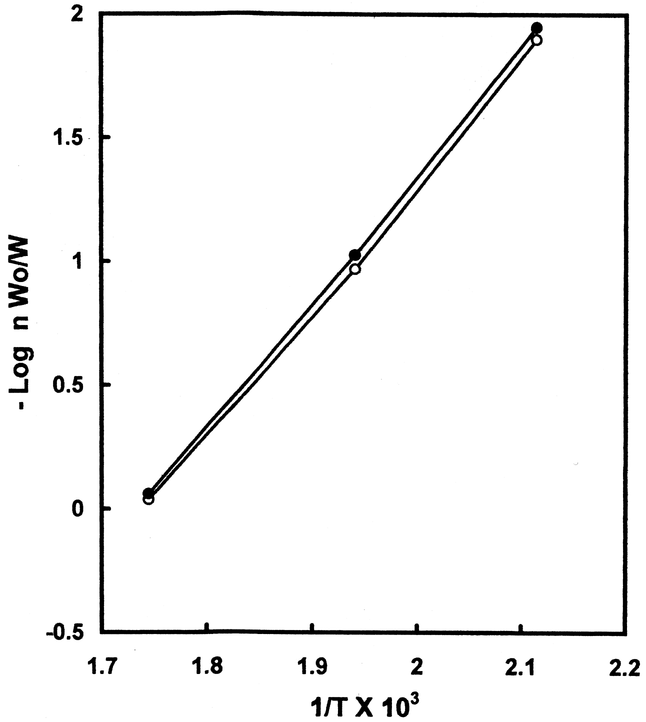

Figure 10. Determination of apparent activation energy for thermal degradation. (o) PVC-g-PAA [1.08%], (·) PVC-g-PAA [2.94%].

CONCLUSION

A maximum grafting of 3.0% of acylic acid onto PVC was obtained using di-(2-phenoxyethyl) peroxy dicarbonate initiator. The percent grafting was low due to the retarding effect of nitrobenzene.

The percent grafting increased with an increase in monomer, initiator concentrations but the intrinsic viscosity decreased.

The thermal stability of graft copolymers increased.

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