

Studies on Graft Copolymerization of Cyclohexyl Methacrylate onto 1,2-Polybutadiene

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Synopsis

The free radical grafting of cyclohexyl methacrylate (CMA) onto 1,2-polybutadiene (1,2-PBD) in benzene solution at 60°C was studied. The graft copolymer was characterized by IR, NMR, DSC, and intrinsic viscosity measurements. The polymerization of CMA shows normal kinetic behavior when the PBD concentration is kept below 1.0 monomer mol/L. The rate of grafting was determined at different reaction times, monomer concentrations, initiator concentrations, backbone concentrations, temperatures, and concentrations of the zinc chloride additive. The performance of the graft copolymer used as adhesive was also investigated for bonding of PVC/PVC film.

INTRODUCTION

The grafting copolymerization of vinyl monomers, such as methyl methacrylate, styrene onto polybutadiene (PBD) with free radical initiators, has been widely studied.¹⁻⁸

Several scholars have intensively investigated the kinetics and mechanism of such chemical modification reaction.¹⁻⁶ For example, Cameron and Qureshi studied the grafting copolymerization of styrene to polybutadiene and reported that the rate of polymerization is independent of PBD concentration.^{1,2} He also described that PBD exerts a pronounced retardation on the polymerization of MMA.⁴ That is, the higher PBD concentration is the lower MMA conversion is obtained. However, copolymerization of PBD and MMA with BPO was also examined by Minoura et al.⁵ They reported that the rate of polymerization was found to be proportional to PBD concentration. This discrepancy may be due to the different reactivity of the MMA toward unreacted PBD radicals and/or the initiator primary radical.

On the other hand, chemical modifications can be devised to give rubber more desirable properties. For example, grafting copolymerization of MMA to natural rubber has been intensively studied and is now a commercially established process for the manufacture of adhesives.⁹

Cyclohexyl methacrylate monomer having the characteristic of good adhesion, yellowing resistance, and good mechanical strength is considered as one of the good modifiers which can be copolymerized with PBD.¹⁰⁻¹⁴

This article presents the results of graft copolymerization of cyclohexyl methacrylate onto 1,2-polybutadiene using BPO as an initiator. Investigations were carried out to study the effects of variations in (1) reaction time,

(2) concentration of monomer, (3) concentration of initiator, (4) concentration of backbone, (5) temperature, and (6) zinc chloride additive effect. Finally, mechanical adhesive property of graft product was also examined.

EXPERIMENTAL

Materials

1,2-Polybutadiene (1,2-PBD) (degree of crystallinity 24.5%, 1,2-PBD contents over 90%, density 0.906, supplied by Japan Synthetic Rubber Co., JSR RB-820) was purified by reprecipitation from their solutions in benzene by methanol.

Cyclohexyl methacrylate (CMA) monomer was prepared by transesterification of methyl methacrylate with cyclohexanol in the presence of *p*-toluene sulfonic acid. It was purified as cyclohexyl acrylate, which has been described before^{15,16} (bp 68°C/4 mm Hg).

Initiator, benzoyl peroxide (BPO), was purified by repeated recrystallization from chloroform. All solvents were purified and distilled before use.

PVC film supplied by the China General Plastics Corp. has a thickness of 0.4 mm.

Polymerization

PBD was dissolved in benzene over a period of 16 h. The ampoule containing CMA, benzene, 1,2-PBD, and BPO was evacuated for several times on a high vacuum system and finally sealed off. Polymerization was thermally carried out at 60°C. The polymer product was precipitated with methanol, purified by reprecipitation from benzene solution with methanol, dried for about 24 h at 60°C under vacuum and weighed.

Separation of Polymers

The gross polymer obtained consists of CMA homopolymer, unreacted PBD, and grafted copolymer. The total polymer cut into thin slices was placed in a weighed Soxhlet thimble. The homopolymer poly(cyclohexyl methacrylate) [poly(CMA)] was removed by extraction with MEK/methanol (2:1 v/v) and the unreacted 1,2-PBD was removed by *n*-hexane/benzene (8:1 v/v) for 48 h. IR techniques have been used to ensure complete removal of nongrafted homopolymer from the grafted products as presented in Figure 1.

The grafting ratio (GR) was calculated as follows:
percent grafting ratio (GR%)

$$= \frac{\text{wt grafted poly(CMA)}}{\text{wt PBD backbone polymer}} \times 100$$

The grafting efficiency (GE) was calculated as follows:
percent grafting efficiency (GE%)

$$= \frac{\text{wt grafted poly(CMA)}}{\text{wt grafted poly(CMA)} + \text{wt of homopoly(CMA)}} \times 100$$

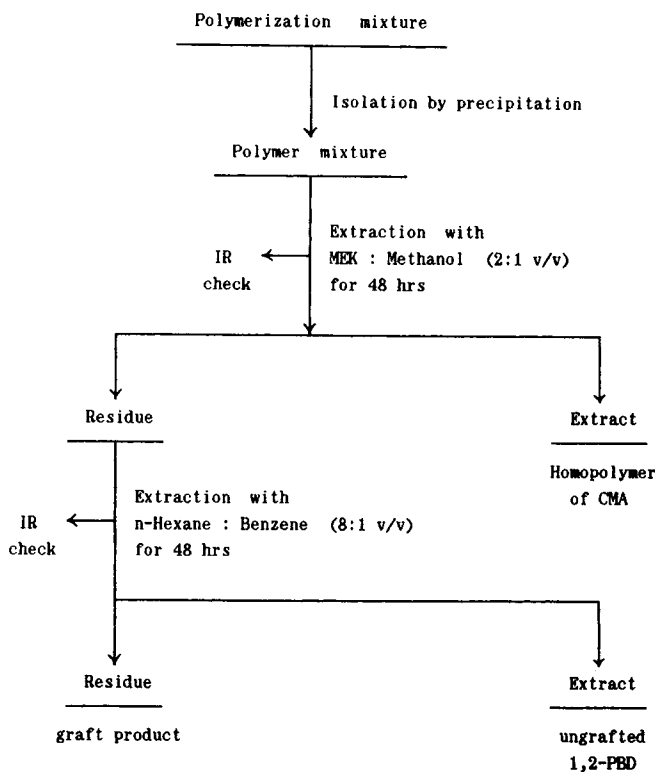


Fig. 1. Separation scheme of 1,2-PBD, homopolymer of CMA and graft products.

The rate of homopolymerization (R_h) and rate of graft copolymerization (R_g) were calculated gravimetrically.

Viscometric Measurements

Viscometric measurements were carried out in benzene with an Ubbelohde viscometer at $30.00 \pm 0.01^\circ\text{C}$.

RESULTS AND DISCUSSION

Polymer Characterization

The grafted polymers were characterized by the measurements of Infrared, $^1\text{H-NMR}$, DSC, and intrinsic viscosity.

Infrared Spectra

Infrared spectroscopy has been found to be a valuable tool in the study of graft copolymerization reactions.^{5,17-23} Figure 2 shows the IR spectra of 1,2-PBD, cyclohexyl methacrylate homopolymer, and graft copolymer. The characteristic band of $\text{C}=\text{O}$ at 1722 cm^{-1} from graft copolymer fraction indicates the presence of acrylate chains. The graft copolymer also shows a strong absorption at 1645 cm^{-1} , which is attributable to residual unsaturation in polybutadiene.

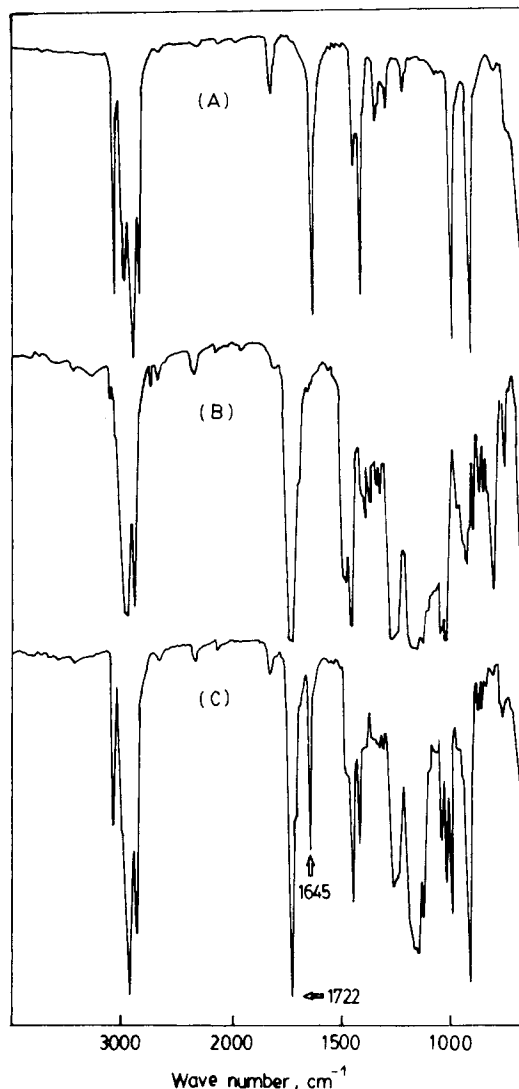
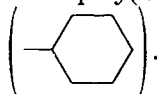


Fig. 2. IR spectra: (A) IR spectrum of 1,2-PBD; (B) IR spectrum of poly(CMA); (C) IR spectrum of CMA-*g*-1,2-PBD copolymer.

NMR Spectra

The NMR spectra of graft polymer taken with TMS as reference standard were examined as shown in Figure 3. From Figure 3(c), the graft polymers with poly(CMA) as side chain showed a broad peak at 1.40–2.50 ppm



. Thus the presence of a side chain polymer was established. A similar study has been examined by other workers.¹⁷⁻¹⁹

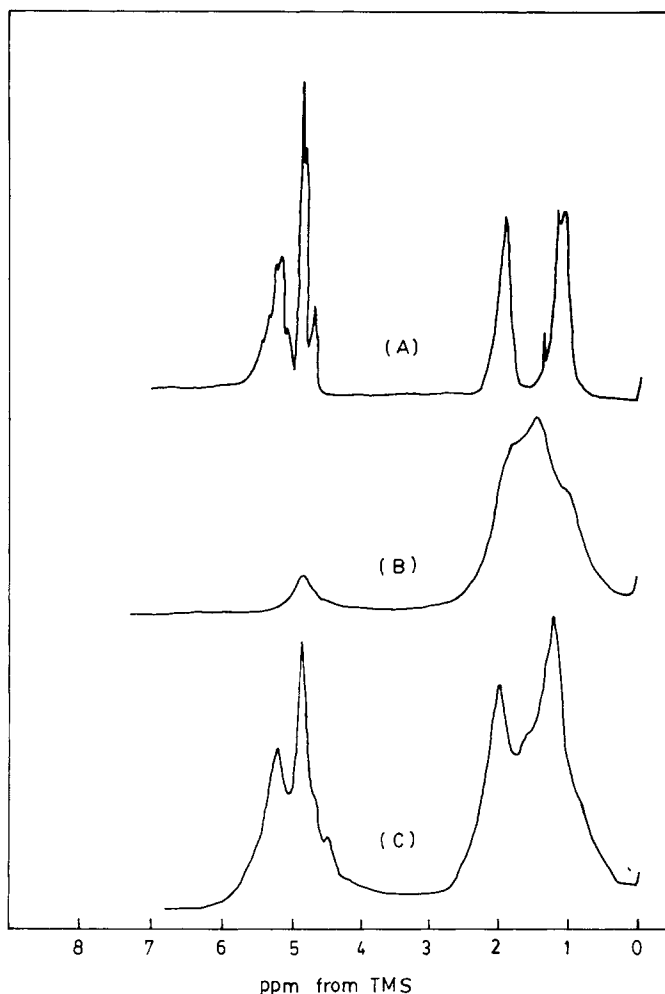


Fig. 3. ¹H-NMR spectra: (A) ¹H-NMR of 1,2-PBD; (B) ¹H-NMR of poly(CMA); (C) ¹H-NMR of CMA-*g*-1,2-PBD copolymer.

Thermal Characterization

Thermal characterization of graft copolymer of cyclohexyl methacrylate with 1,2-PBD was carried out by DSC. Only one glass transition temperature (T_g) was found. The glass transition temperature of graft copolymer was found to be 276 K, which is between that of 1,2-PBD (248 K)²⁴ and poly(CMA) (356 K)²⁵ as shown in Figure 4 and Table I. However, DSC scans showed that T_g was not evidently found for the blends of PBD and poly(CMA).

Viscosity Measurement

Another evidence for the graft copolymerization is the measurement of intrinsic viscosity. Table II shows the result for the various polymer including

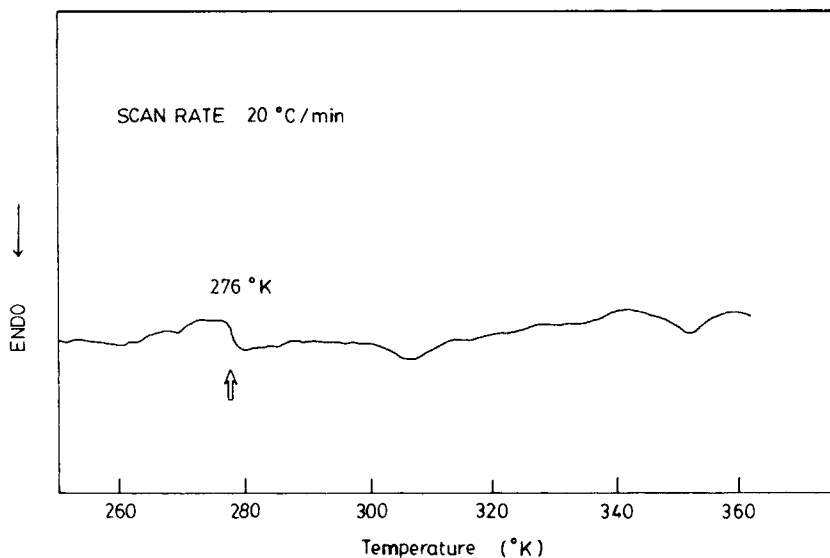


Fig. 4. DSC scan of CMA-g-1,2-PBD copolymer.

TABLE I
DSC Data of Transition Temperature of Various Polymers^a

Polymer	T_g (K)	Reference
1,2-PBD	248	24
Graft product	276	This work
Blending of 1,2-PBD and poly(CMA)	Not detected	This work
Poly(CMA)	356	25

^aScanning rate 20°C/min; temperature range: 260–360 K.

graft copolymer, blending product, and homopolymers for 1,2-PBD and poly(CMA). The intrinsic viscosity of graft copolymer is the highest in comparison with that of blending products.

From the characterization mentioned above, three types of the graft copolymerization could be suggested. That is, the initiator radical ($R\cdot$) first attacks

TABLE II
The Intrinsic Viscosity [η] of Various Polymers^a

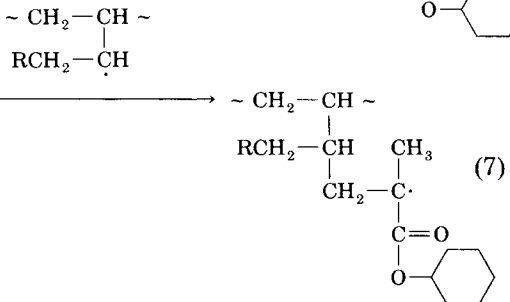
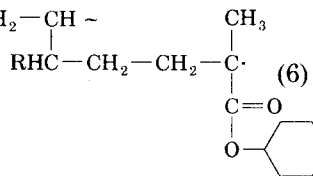
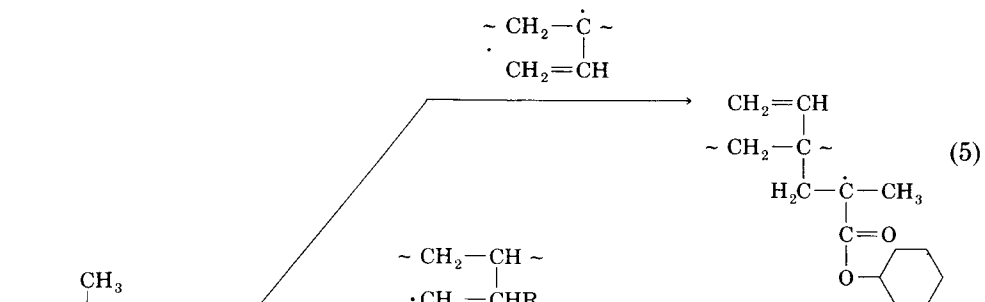
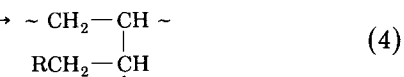
Polymer	[η] (dL/g)
1,2-PBD	1.52
Graft product ^b	1.71
Blending of 1,2-PBD and poly(CMA) ^c	1.39
Poly(CMA)	1.19

^aSolvent, benzene; temperature, 30.00 ± 0.01°C.

^bGrafting ratio, 50 wt %.

^cWeight of poly(CMA) in blending product, 50%.

PBD by the addition and/or hydrogen transfer. Then, cyclohexyl methacrylate monomer attacks PBD radicals as shown in the eqs. (1)–(7):



Determination of Kinetic Order

The rate of polymerization (R_p) has been measured at five different monomer concentration within the range of 0.2–2M at 60°C. The rate of polymerization increases with increasing monomer concentration. The plot of R_p vs. $[M]$ is linear (Fig. 5), indicating that the order with respect to monomer is unity. Similar results have been reported by several workers for the polymerization of methyl methacrylate.^{1, 4, 5, 19, 26–30}

The influence of benzoyl peroxide (BPO) on R_p was studied at 60°C as shown in Figure 6. The plots of R_p vs. $[BPO]^{1/2}$ are linear, indicating that the rate of polymerization was the square root of the initiator concentration. This result suggests that bimolecular termination occurs in the polymerization

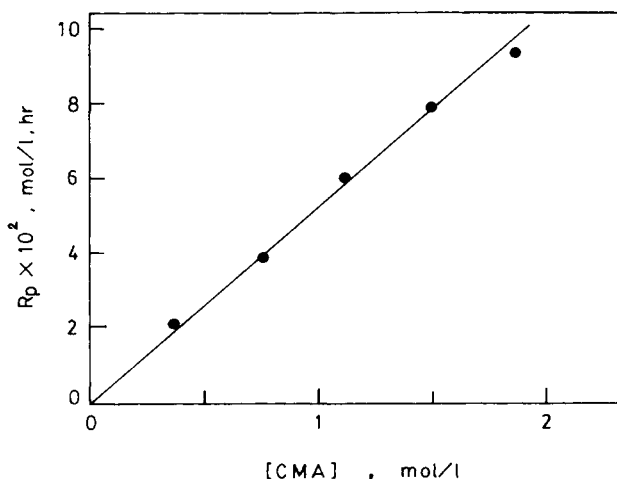


Fig. 5. Rate of polymerization vs. monomer concentration: $[1,2\text{-PBD}] = 0.40$ mol/L; $[BPO] = 2.75 \times 10^{-3}$ mol/L; temp, 60°C.

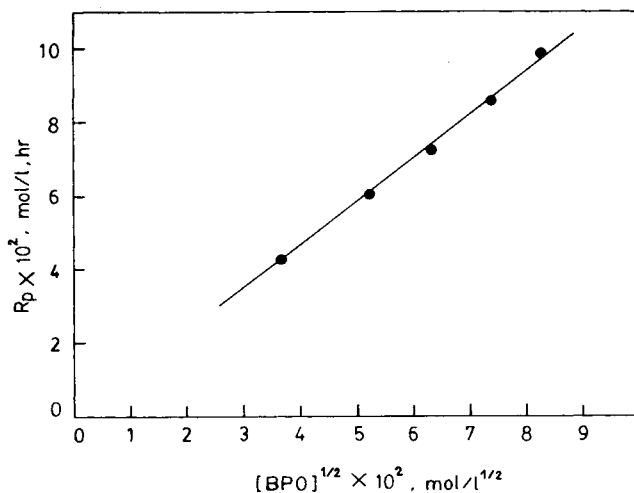


Fig. 6. Rate of polymerization vs. initiator concentration: $[1,2\text{-PBD}] = 0.40$ mol/L; $[CMA] = 1.14$ mol/L; temp, 60°C.

process. Thus, the polymerization of cyclohexyl methacrylate shows normal kinetic behavior when the PBD concentration is kept below 1.0 monomer mol/L. A similar order was also noted by several workers for the polymerization of methyl methacrylate.^{4,5}

Effect of Reaction Time

Various experiments were conducted in order to understand the nature of graft copolymerization onto polybutadiene. The effects of time, temperature, monomer concentration, initiator concentration, polybutadiene concentration, and zinc chloride additive were studied. The grafting of CMA onto PBD was studied as a function of time, and the results are given in Table III. With the increase in grafting reaction time, grafting ratio was found increasing. On the other hand, the grafting efficiency was kept constant near 50%, indicating that the rate of grafting (R_g) was almost equal to that of homopolymerization (R_h) during polymerization.

Effect of Monomer Concentration

Effect of monomer concentration on grafting was shown in Table IV. The rate of grafting increases with increasing monomer concentration up to 1.52 M. With further increase of the monomer, the rate of grafting decreases. The increase in monomer concentration from 0.38 to 1.52 mol/L decreases grafting efficiency but increases grafting ratio. From this, it could be stated that the

TABLE III
Effect of Reaction Time on Grafting^a

Time (h)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
1	3.00	3.20	48.3	23.3
2	2.93	3.08	48.8	45.6
3	3.08	3.17	49.3	71.9
4	3.03	3.14	49.1	94.2
5	3.03	3.19	48.7	118.0

^a[1,2-PBD] = 0.40 mol/L; [CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L; temp, 60°C; solvent, benzene; total vol, 15 mL.

TABLE IV
Effect of Monomer Concentration on Grafting^a

CMA concn (mol/L)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
0.38	1.52	0.78	66.1	17.7
0.76	2.10	1.88	52.7	24.5
1.14	2.95	3.15	48.4	34.4
1.52	3.17	4.84	39.6	37.0
1.90	2.87	6.63	30.2	33.4

^a[1,2-PBD] = 0.40 mol/L; [BPO] = 2.75×10^{-3} mol/L; temp, 60°C; reaction time, 1.5 h; solvent, benzene; total vol, 15 mL.

rate of homopolymerization increases more remarkably than that of grafting as monomer concentration increase.

Effect of Initiator Concentration

Benzoyl peroxide (BPO) was found to be an efficient initiator for grafting of vinyl monomers onto polybutadiene. In the present investigation, the initiator concentration varied from 1.38×10^{-3} to 6.89×10^{-3} mol/L. As Table V shows, both the grafting ratio and the rate of grafting increase with the increase of initiator concentration. On the other hand, the graft efficiency is kept constant. This is due to the fact that homopolymerization is favored in higher initiator concentration. Moreover, when the initiator concentration is over 8×10^{-3} mol/L, crosslinking reaction occurred.

Effect of Backbone Concentration

The variation of polybutadiene concentration has a profound effect on the grafting efficiency and grafting ratio as seen in Table VI. The grafting ratio decreases with increasing backbone concentration. The rate of grafting increased initially with increase in polybutadiene concentration, then reached a maximum value, and finally decreased with further increase in polybutadiene concentration. However, the PBD concentration is beyond 1.0 monomer mol/L; gel formation was observed.

TABLE V
Effect of Initiator Concentration on Grafting^a

BPO $\times 10^3$ (mol/L)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
1.38	2.07	2.21	48.4	32.2
2.75	2.96	3.13	48.6	46.0
4.13	3.50	3.79	48.0	54.4
5.50	4.14	4.45	48.2	64.4
6.89	4.80	5.08	48.6	74.6

^a[1,2-PBD] = 0.40 mol/L; [CMA] = 1.14 mol/L; temp, 60°C; reaction time, 2 h; solvent, benzene; total vol, 15 mL.

TABLE VI
Effect of 1,2-PBD Concentration on Grafting^a

1,2-PBD concn (monomer mol/L)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
0.23	2.63	4.75	35.6	89.0
0.31	2.82	3.95	41.7	70.8
0.49	3.08	3.08	50.0	48.9
0.69	2.96	2.24	57.0	33.4
0.90	2.66	1.51	63.8	23.0

^a[CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L; temp, 60°C; reaction time, 2.5 h; solvent, benzene; total vol, 15 mL.

Effect of Temperature

The graft copolymerization was carried out at four different temperatures over the range 50–80°C, keeping the concentrations of all other reagents constant as shown in Table VII. There is a regular increase in grafting ratio, grafting efficiency, rate of homopolymerization, and rate of grafting with increasing temperature. From the Arrhenius plot of $\log R_p$ vs. $1/T$, the overall activation energy was computed to be 80.3 kJ/mol, as shown in Figure 7.

Effect of Zinc Chloride

The effect of zinc chloride on the grafting is shown in Figure 8 and Table VIII. Figure 8 shows the maximum grafting efficiency as zinc chloride concentration is 0.1 mol/L. From Table VIII it was observed that, with increase of zinc chloride concentration up to 0.4 mol/L, the rate of grafting and the grafting ratio increase. This fact may be due to the complex formation that enhances the rates of both grafting polymerization and homopolymerization

TABLE VII
Effect of Temperature on Grafting^a

Temperature (°C)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
50	1.22	1.82	40.1	14.2
60	2.95	3.13	48.5	34.4
70	7.76	5.98	56.5	90.5
80	22.81	12.73	64.2	266.1

^a[1,2-PBD] = 0.4 mol/L; [CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L; reaction time, 1.5 h; solvent, benzene; total vol, 15 mL.

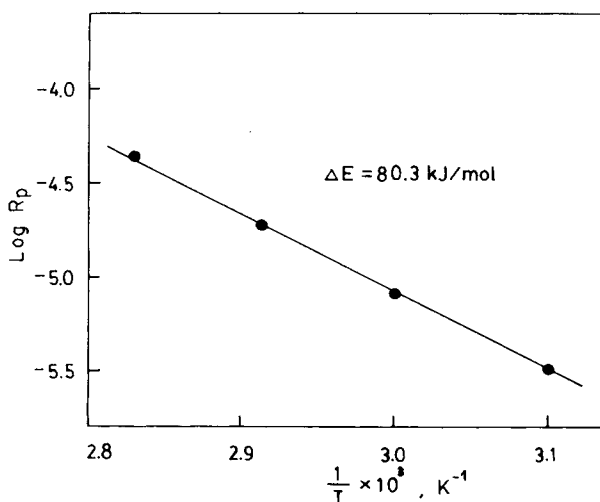


Fig. 7. Arrhenius plot of $\log R_p$ vs. $1/T$: [1,2-PBD] = 0.40 mol/L; [CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L.

TABLE VIII
Effect of Zinc Chloride Concentration on Grafting^a

ZnCl ₂ concn (mol/L)	$R_g \times 10^2$ (mol/L h)	$R_h \times 10^2$ (mol/L h)	GE (%)	GR (%)
0	2.95	3.13	48.3	22.9
0.1	5.21	3.34	60.9	40.5
0.2	6.51	6.08	57.8	50.6
0.3	6.84	7.04	49.3	53.2
0.4	7.21	9.00	44.4	56.1
0.5	6.30	11.94	34.5	49.0

^a[1,2-PBD] = 0.40 mol/L; [CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L; reaction time, 1 h; temp, 60°C; solvent, benzene; total vol, 15 mL.

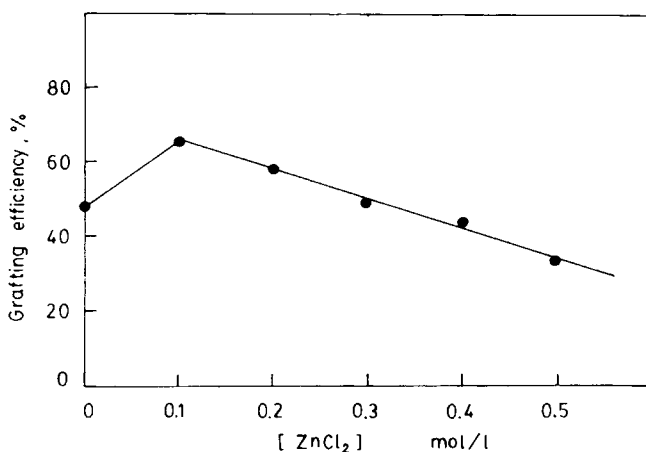


Fig. 8. Effect of zinc chloride concentration on the grafting efficiency of CMA: [1,2-PBD] = 0.40 mol/L; [CMA] = 1.14 mol/L; [BPO] = 2.75×10^{-3} mol/L; reaction time, 1 h; temp, 60°C.

between zinc chloride and carbonyl group of cyclohexyl methacrylate.^{15,16} The carbonyl peak was shifted from 1722 to 1682 cm^{-1} due to the complex formation. When the zinc chloride concentration increases beyond 0.4 mol/L, the rate of grafting decreases, as shown in Table VIII.

Adhesive Application

One of the most effective applications for graft copolymer is to perform to use as a film adhesive. Cyclohexyl methacrylate is considered to be a good modifier with which polybutadiene could be grafted. Table IX shows the peel strength in various adhesives for bonding plasticized poly(vinyl chloride). From Table IX it is clear that the peel strength of graft copolymer is higher than that of the blending product. In addition, the adhesive for the graft copolymer of CMA is more effective than that of MMA as shown in Table IX.

Figure 9 shows the dependence of peel strength on the grafting ratio of graft products for bonding of PVC/PVC. From Figure 9, it is seen that the adhesion of the CMA-*g*-PBD is superior to that of MMA-*g*-PBD at any grafting ratio. This result is consistent with Table IX. The graft copolymer

TABLE IX
Peel Strength of Graft Products as Adhesive for Bonding of Poly(vinyl Chloride)^a

Adhesives	Peel strength (kN/m)
1,2-PBD	0.04
CMA-g-1,2-PBD copolymer ^b	5.30
Blending of 1,2-PBD and poly(CMA) ^c	0.49
Poly(CMA)	0.93
MMA-g-1,2-PBD copolymer ^b	4.00
Blending of 1,2-PBD and poly(MMA) ^d	0.28
Poly(MMA)	0.72

^a Polymer content, 10 wt % in toluene.

^b Grafting ratio, 50%.

^c Weight of poly(CMA) in blending product, 50%.

^d Weight of poly(MMA) in blending product, 50%.

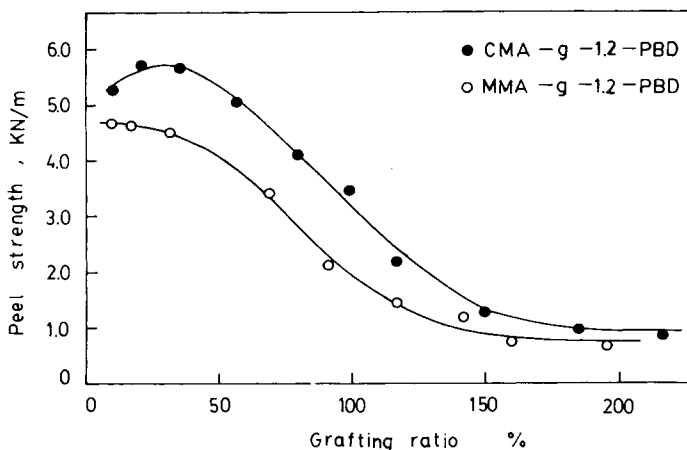


Fig. 9. Dependence of peel strength on the grafting ratio of graft products for bonding of PVC/PVC; (●) CMA-g-1,2-PBD; (○) MMA-g-1,2-PBD.

for CMA having 20–30% of grafting ratio was confirmed to be an effective adhesive for bonding of plasticized poly(vinyl chloride).

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Received March 16, 1988

Accepted March 18, 1988