Studies on Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Poly(vinyl chloride)

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SYNOPSIS

Poly(vinyl chloride) was dehydrochlorinated in alkali solution and then grafted with 2-hydroxyethyl methacrylate (HEMA) using benzoyl peroxide as a free-radical initiator under a nitrogen atmosphere. The investigations involved examining the effects of grafting efficiency on various conditions, such as degree of dehydrochlorination, HEMA concentration, solvent effect, and reaction time. Maximum grafting to the extent of 57.2% was obtained. The mixed solvent grafting was attempted. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The grafting copolymerization of vinyl monomers such as styrene and acrylates onto poly(vinyl chloride) has been widely studied.[1-6,11-20] Those graft methods that commonly used dehydrochlorination or γ-irradiation have been reported in previous literature.[1-20] Hydrophillic monomer grafting was investigated by several scholars.[1-9] For example, Kraishan and Kraishan, Goldberg and Vahiaoui and Singh et al., respectively, investigated the grafting of *N*-(vinyl pyrrolidone) (NVP), 2-hydroxyethyl methacrylate (HEMA), and methacrylic acid grafted onto medical grade PVC sheets by UV or γ-irradiation.[1-3] Vigo and Uliana investigated vinyl acetate and HEMA grafted onto PVC via chemical and radiation methods.[4,5] Sankholkar and Deb proved the method of grafting a methyl methacrylate–methacrylic acid monomer pair onto poly(vinyl chloride) (PVC) and chlorinated rubber.[6] Lai et al. also studied HEMA and other vinyl monomers grafted onto nylon 4 membrane.[7-9] These hydrophillic grafted copolymers were applied toward asymmetrically ultrafiltration membranes and medical applications such as blood circulation applications. The above grafting reactions were employed in a heterogeneous system using a radiation method. Investigating the grafting of hydrophillic acrylate monomers in homogeneous procedure would therefore be a worthwhile research task.

This article presents the results of graft copolymerization of HEMA onto dehydrochlorinated poly(vinyl chloride) (DHPVC) using benzoyl peroxide (BPO) as a free-radical initiator to give grafted copolymer with a hydroxy group. Investigations were carried out here for examining the effects of variations in reaction time, concentration of monomer, and dehydrochlorination at various concentrations of NaOH.

EXPERIMENTAL

Materials

PVC resin (S-70, degree of polymerization [D_p] = 1070) was supplied by Formosa Plastic Co. (Taiwan). HEMA was distilled under reduced pressure. BPO was purified by dissolving in chloroform at room temperature and precipitating by the addition of methanol. Cyclohexanone, tetrahydrofurfuryl alcohol, and NaOH were used as received. Commercial *n*-hexane was distilled and used as a precipitant.

Preparation of Dehydrochlorinated PVC (DHPVC)

A weighed quantity of PVC resin and 10 times its amount of 10% NaOH solution in mass were fed into a round-bottom flask fitted with a reflux con-

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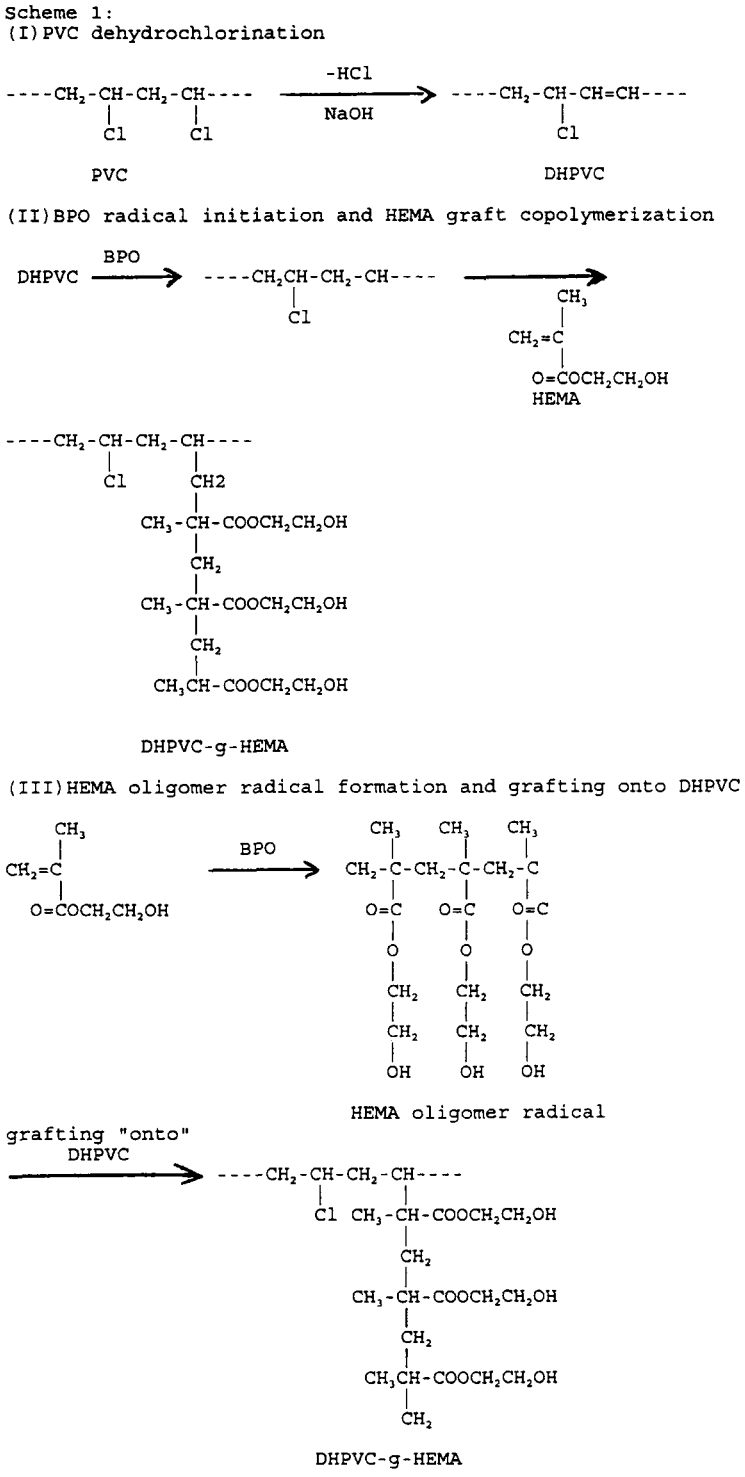
Journal of Applied Polymer Science, Vol. 51, 2175–2186 (1994)
 CCC 0021-8995/94/132175-12



Scheme 1

denser. Dehydrochlorination proceeded for 2 h at 100°C. The dehydrochlorinated material in each case was washed with distilled water until removal of all traces of alkali and then dried under a vacuum for at least 8 h. The reddish product is referred to as dehydrochlorinated PVC (DHPVC).

Graft Polymerization and Separation

The graft polymerization is shown in Scheme 1. First, DHPVC (5 g) and solvent (50 g) were left overnight for complete dissolution; the solution was then stirred and heated to 70°C under a nitrogen atmosphere. When the desired temperature was reached, HEMA monomer (a known amount containing BPO 1.5×10^{-4} mol/g DHPVC) was added with continuous stirring at 70°C. The reaction was carried out for predetermined periods. The mixture was then cooled and poured into an excess well-stirred *n*-hexane. The precipitated polymer was filtered and washed several times with *n*-hexane and then dried to a constant mass at 50°C under vacuum. The precipitate was a mixture of grafted copolymer PVC-*g*-HEMA and poly(HEMA). Poly(HEMA) was removed by Soxhlet extraction with methanol as a solvent. The remaining solid PVC-*g*-HEMA was dried under vacuum and weighed. The filtrate [a solution of poly(HEMA) in methanol] was concentrated by a rotary vacuum evaporator; the residue was precipitated with distilled water. The recovered poly(HEMA) was dried and weighed.

Estimation of Grafting Parameters

Gravimetry

The grafting parameters were estimated from the mass of the sample before and after grafting. The fraction of grafting and the grafting efficiency were calculated according to the relationships

$$\text{Fraction of grafting} = \frac{\text{mass of grafted poly (HEMA)}}{\text{mass of grafted copolymer}} \times 100\%$$

$$\text{Grafting efficiency} = \frac{\text{mass of poly (HEMA) in graft}}{\text{(mass of poly (HEMA) in graft + mass of poly (HEMA) homopolymer)}} \times 100\%$$

Chlorine Estimation

This method was applied toward the chlorine analysis of the sample through an elemental analyzer (Tacussel Coulomax 78) with 1-chloro-2,4-dinitro-

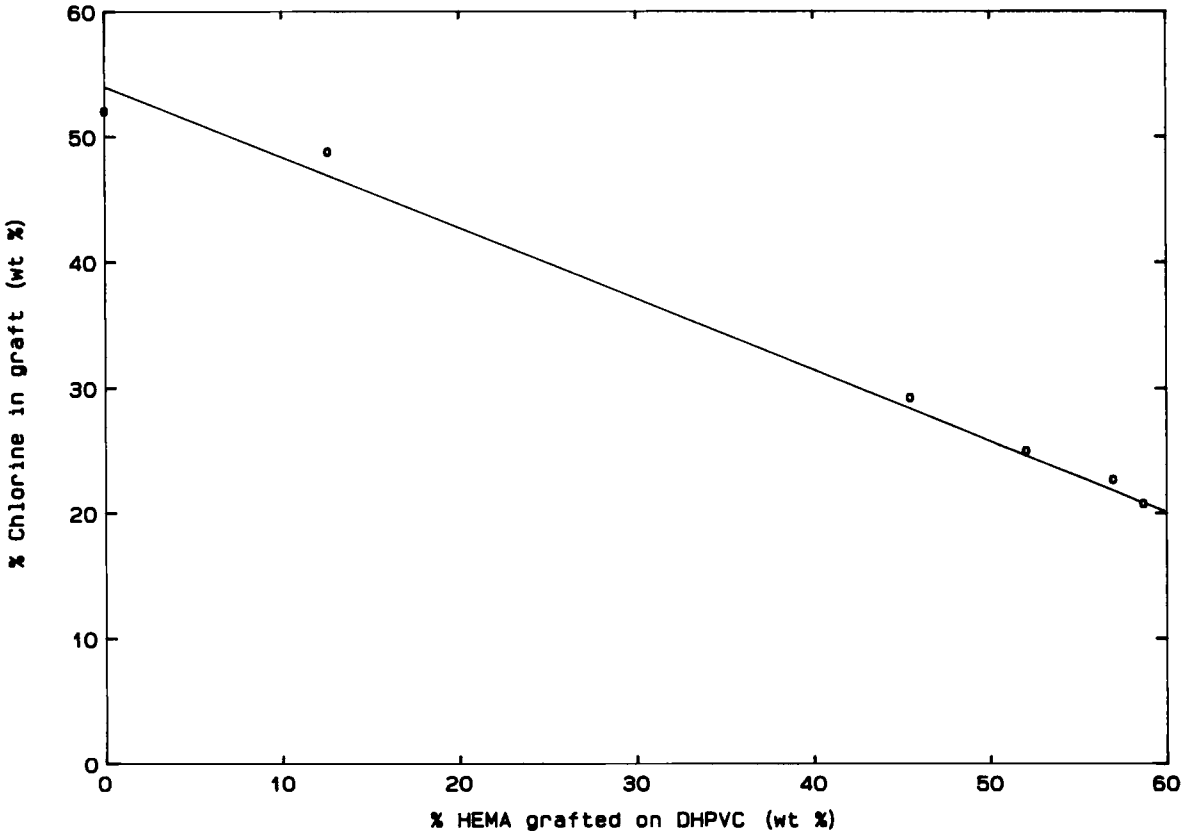


Figure 1 Relationship between fraction of grafting and content of chlorine.

benzene used as the standard. The calibration curve for the mass fraction of chlorine of various grafted copolymers vs. weight percent poly(HEMA) grafting is plotted in Figure 1. This curve can be used for calculating the weight fraction of HEMA on grafted samples.

Characterization Techniques

IR spectra of solvent-cast films were measured on the spectrophotometer (Jasco FT/IR-7000) in the range 400–4600 cm^{-1}. DSC was carried out on a differential scanning calorimeter (DuPont Instruments 9900) at a heating rate of 10°C/min in the range 20–160°C.

RESULTS AND DISCUSSION

Characterization of Graft Copolymer

The IR spectra of PVC, poly(HEMA), and various grafted copolymers are exhibited in Figure 2. In contrast to PVC, the grafted copolymer displayed two new absorption peaks at 1725 cm^{-1} and 3426 cm^{-1}. These peaks indicate the introduction of the carbonyl and hydroxy groups of HEMA. The plot of the ratio $\nu_{C=O,1725\ cm^{-1}}/\nu_{C-Cl,636\ cm^{-1}}$, which is calculated by shoulder method vs. the fraction of HEMA grafting, is illustrated in Figure 3. As the fraction of the HEMA grafted onto PVC linearly increased, the intensity ratio of specific peak was increasing. Such a result would consequently offer a method to estimate the fraction of grafting of copolymer.

The glass transition temperatures (T_g) of PVC, poly(HEMA), and various fractions of grafting PVC-*g*-HEMA are exhibited in Table I. T_g of poly(HEMA) is nearly 15°C larger than that of PVC. Consequently, the T_g of grafted copolymers increased with an increase of the HEMA fraction on grafted copolymers. T_g obtained from DSC method was fitted well with those estimated by the Fox equation.

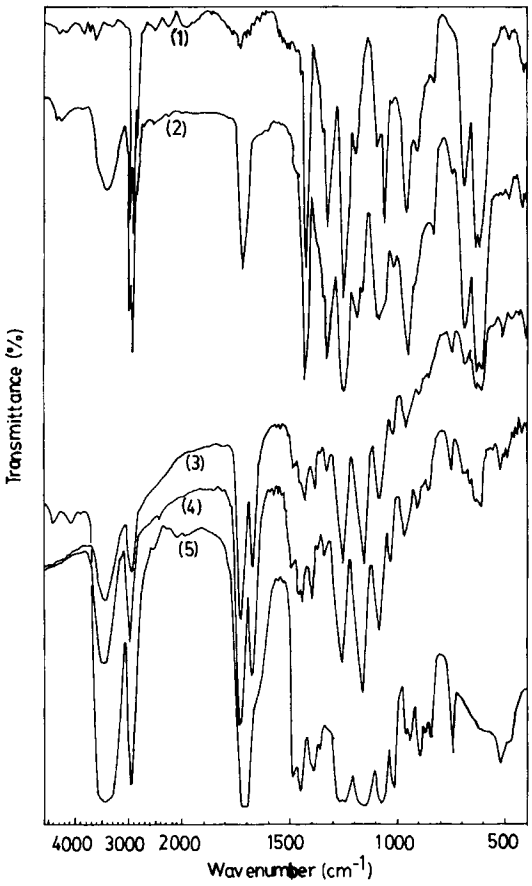


Figure 2 IR spectra of PVC, poly(HEMA), and various fractions of grafted PVC-*g*-HEMA: (1) PVC; (2) 13.0% grafted; (3) 41.5% grafted; (4) 56.9% grafted; (5) poly(HEMA).

Effect of Degree of Dehydrochlorination by Various Concentrations of Alkali on Fraction of Grafting

The influence of degree of dehydrochlorination on HEMA grafting is illustrated in Figure 4. The fraction of grafting and grafting efficiency increased with an increase in NaOH concentration. The more active sites on PVC would be created for the more alkali quantity provided. This is the result of an increasing in the fraction of grafting and grafting efficiency. The plot of NaOH concentration vs. mass faction of chlorine in DHPVC is demonstrated in Figure 5. The relationship shown in Figure 5 indicates that the stronger alkali actually created more hydrochloride to be removed, i.e., more active sites in PVC main chains would be generated. The same result had been obtained in our report.[20]

Effect of the HEMA Monomer Concentration on the Fraction of Grafting

The effect of the content of HEMA monomer concentration on the fraction of grafting and grafting efficiency was examined in the range $0.5–2.0 \times 10^{-2}$ mol/g DHPVC. A continuous increase in the fraction of grafting and decrease in grafting efficiency

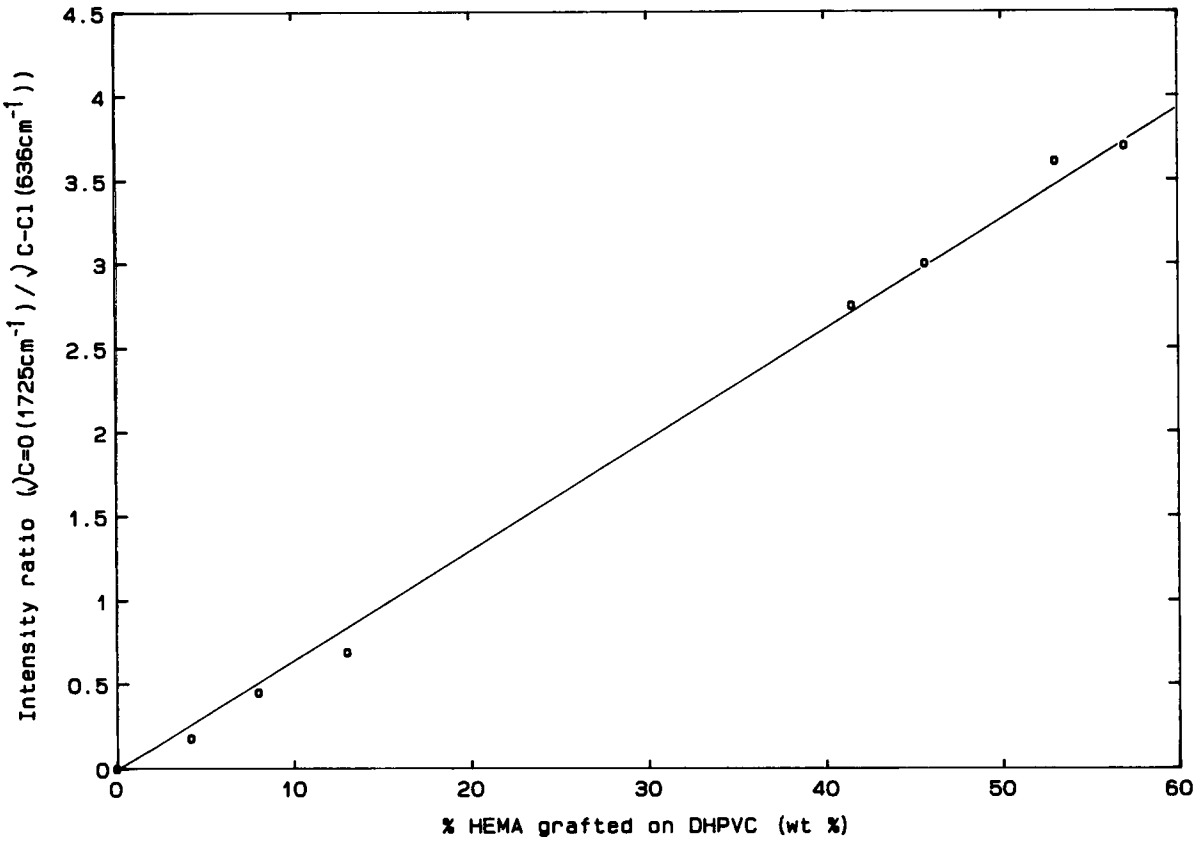


Figure 3 Fraction of grafting of HEMA grafted on PVC vs. intensity ratio $\nu_{C=O(1725\ cm^{-1})}/\nu_{C-Cl(636cm^{-1})}$ from IR spectra.

with increasing HEMA concentration are shown in Figure 6. This phenomenon had been previously reported by Vigo and Uliana,[4] who studied PVC grafted vinyl acetate, and by Lai et al., who studied nylon 4-grafted HEMA.[9] Most monomers would apparently become poly(HEMA), especially in a high concentration region. The low fraction of grafting indicated that HEMA would apparently be difficult to be grafted onto DHPVC although active sites were sufficient. Employing a high HEMA concentration so as to raise the fraction grafting would therefore be impossible.

Table I The Glass Transition Temperature of PVC, Various Fractions of Grafting of PVC-*g*-HEMA, and Poly(HEMA)

Sample	Grafting (%)	T_g (K) (by DSC)	T_g (K) (by Fox eq.)
PVC	—	354.89	—
PVC-*g*-HEMA	13.0	356.45	356.61
PVC-*g*-HEMA	41.5	357.75	360.37
PVC-*g*-HEMA	45.7	360.62	360.91
PVC-*g*-HEMA	53.0	360.97	362.09
Poly(HEMA)	—	368.56	—

Effect of Reaction Time

The consequence of grafting reaction time in cyclohexanone is demonstrated in Figure 7. The curves displaying a maximum value in reaction time of 3 h are divided into two parts from the maximum point. In the prior period, the fraction of grafting and grafting efficiency was elevated until the reaction time of 3 h. The chain transfer of the grafted side chain on PVC occurred by the descendent curve from 3–6 h. This occurrence is similar to the GMA-grafted PVC reported in previous paper[20] and U. K. Saroop PVC grafted MMA.[17]

The conversion of HEMA overall polymerization (C_p), grafting copolymerization (C_g), and homopolymerization (C_h) through the whole process are

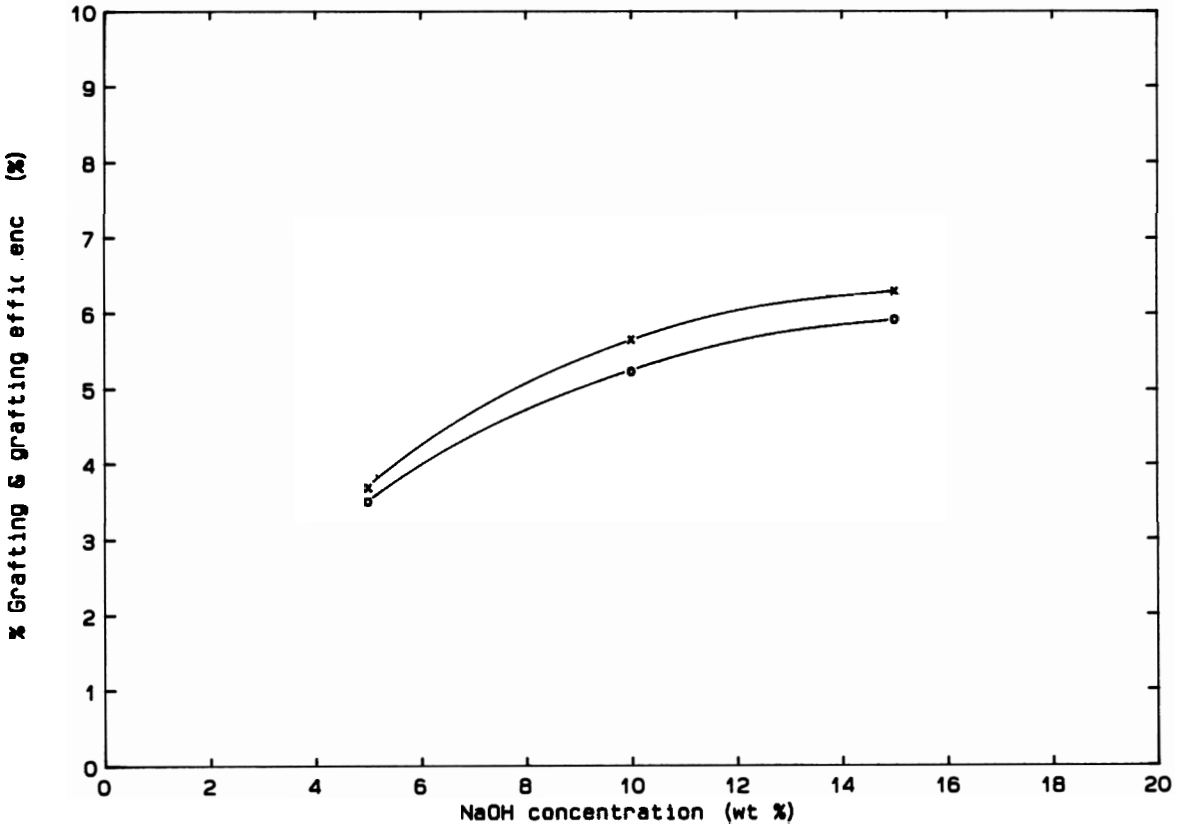


Figure 4 Effect of PVC dehydrochlorinated at various concentrations of NaOH in the grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. HEMA concentration 1.5×10^{-2} (mol/g) DHPVC; reaction time: 3 h.

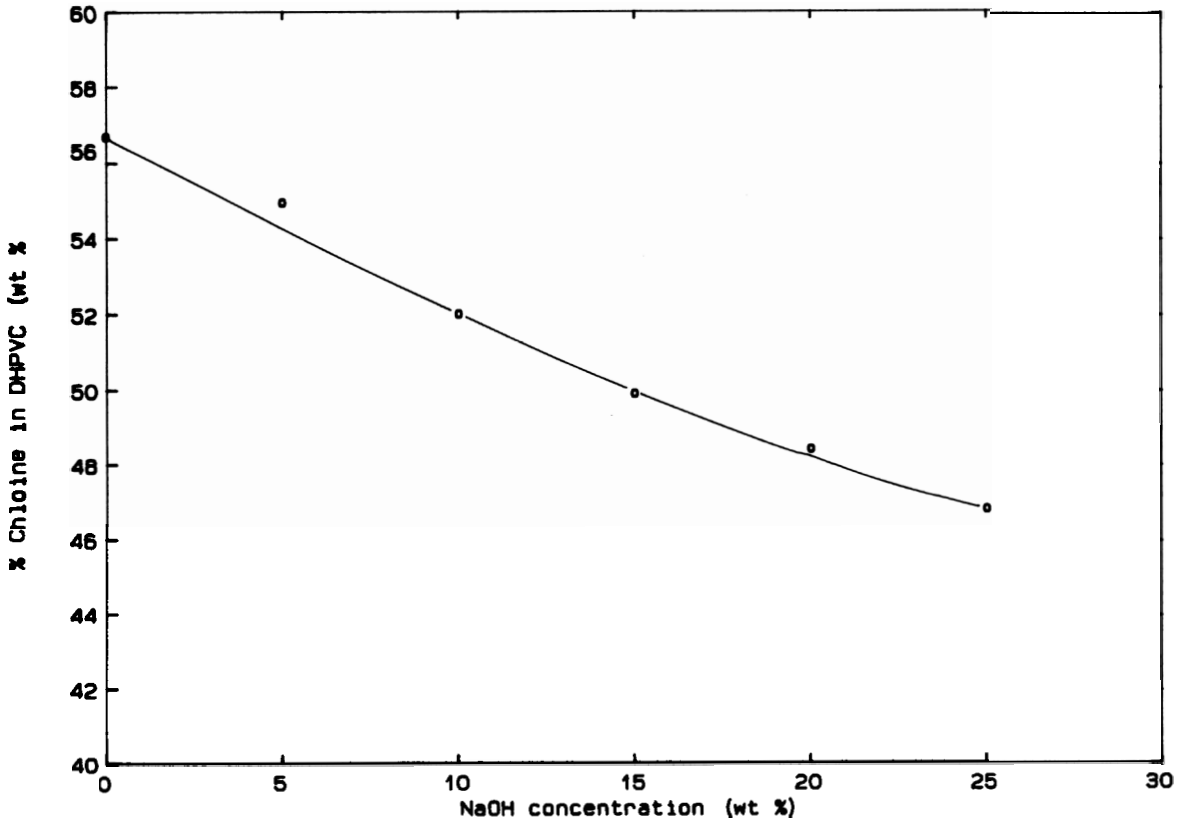


Figure 5 Relationship between dehydrochlorinating alkali concentration and content of chlorine in DHPVC.

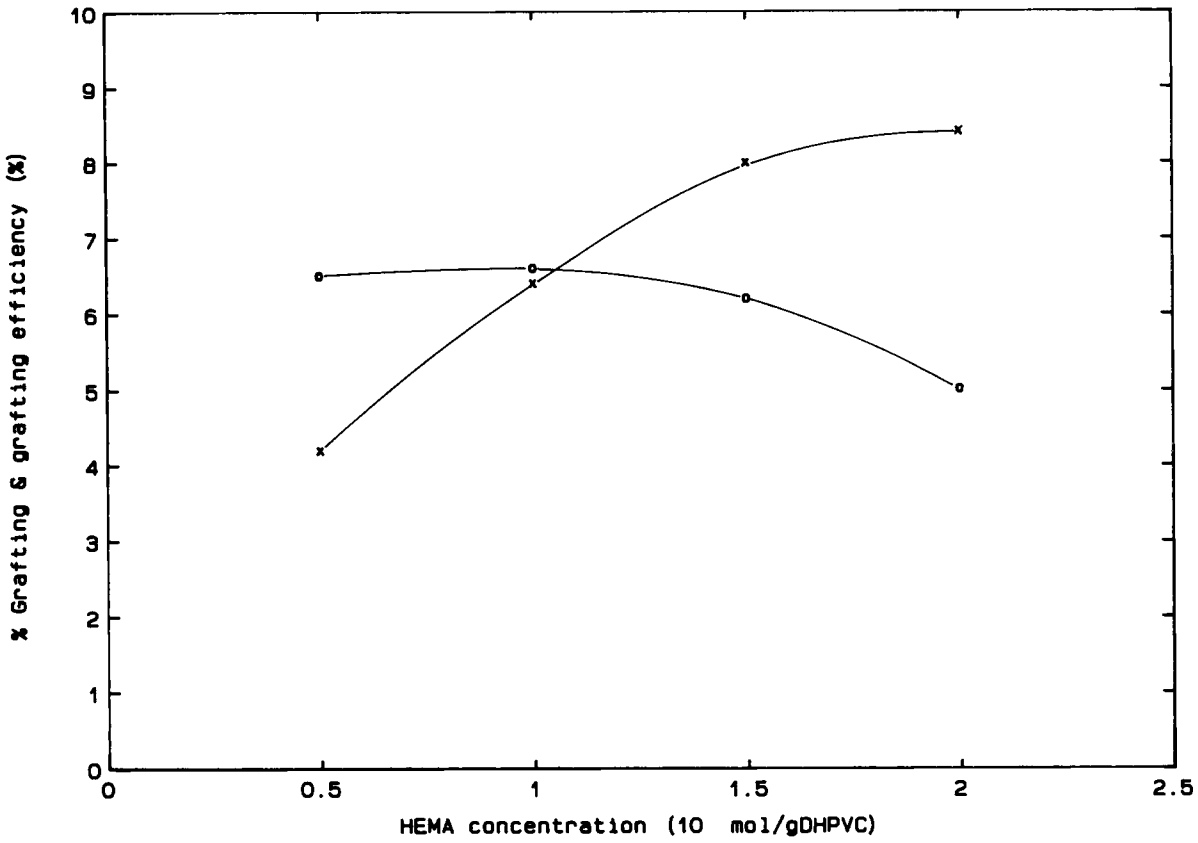


Figure 6 Effect of HEMA concentration in grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. 10% NaOH-treated DHPVC; reaction time: 3 h.

demonstrated in Table II. The overall conversion of HEMA polymerization (C_p) increased with an increasing reaction time. This occurrence meant that the decomposition of initiator was fast during the initial period of reaction. An enormous amount of free radicals generated favored the probability of polymerization during the initial period. The conversion of homopolymerization (C_h) was obviously larger than that of grafting polymerization. Most HEMA monomer had the tendency of becoming homopolymer. This result was also observed in the GMA grafted copolymerization from our previous work.[20]

Table II HEMA Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Cyclohexanone[a]

Time (h)	C_p (%)	C_g (%)	C_h (%)
1	42.53	2.74	39.79
2	67.48	4.22	63.26
3	84.84	5.28	79.56
4	91.08	3.68	87.40
5	95.50	2.10	93.40
6	95.40	1.14	94.26

[a] Ten percent NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC.

Solvent Effect

The low fraction of grafting indicated that the graft copolymerization in cyclohexanone was difficult. This difficulty was a consequence of cyclohexanone being a poor solvent of poly(HEMA) according to the solubility parameter. The long HEMA radical chain did not easily attack the active sites on PVC chain during graft reaction. Finding a solvent which both correlates with PVC and poly(HEMA) is important for both resolving this problem and also enhancing the fraction of grafting. Such a single solvent had, unfortunately, not been found after di-

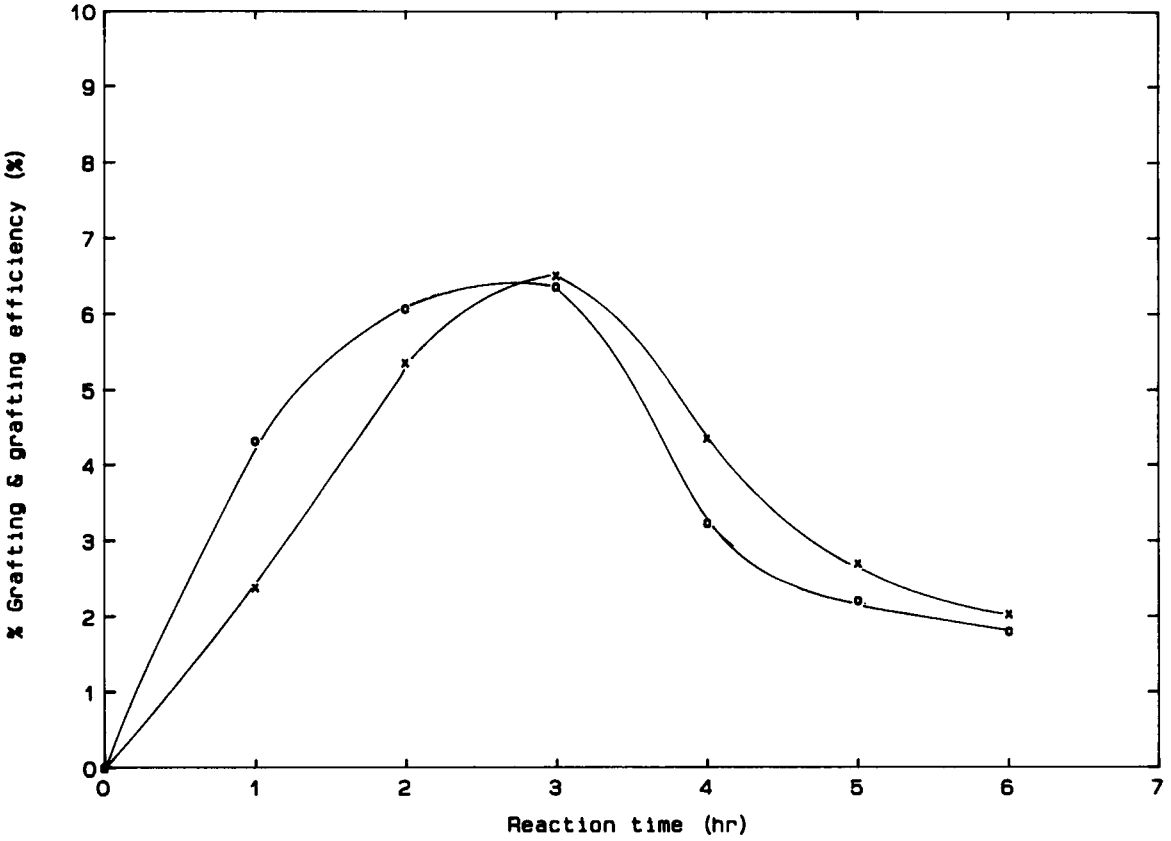


Figure 7 Effect of reaction time in the cyclohexanone grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. 10% NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC.

rectly testing and consulting the present references. However, a mixed solvent was considered for resolving this problem. Tetrahydrofurfuryl alcohol mixed with cyclohexanone was chosen as the graft solvent. A half-quantity of DHPVC (2.5 g) was employed since 5 g DHPVC did not become completely dissolved in the mixed solvent. The result of the mixed solvent effect in the fraction of grafting (see Fig. 8) exhibited a small increase with increase of tetrahydrofurfuryl alcohol. However, a higher fraction of grafting and grafting efficiency had been successfully acquired compared with that of the pure cyclohexanone system. The hydroxyl group in tetrahydrofurfuryl alcohol actually made a contribution to the grafting but not significantly. Another important factor was found accidentally. The fraction of grafting and grafting efficiency for a half-amount of HEMA/DHPVC (2.5 g DHPVC) was more highly elevated than that for the 5.0 g DHPVC system in pure cyclohexanone. This phenomena implied that the DHPVC concentration was perhaps a major factor of HEMA grafting in this system.

Effect of Reaction Time in Mixed Solvent

The possibility of a high fraction of grafting of the HEMA copolymer had been acquired in a cyclohexanone/tetrahydrofurfuryl alcohol mixed solvent and the influence of reaction time should be examined. The equal ratio of mixed solvent (50:50, wt %) was chosen as the graft solvent and its outcome is exhibited in Figure 9. The fraction of grafting exhibited in Figure 9 did not decrease after a particular reaction time; additionally, the fraction of grafting did not significantly increase after the period of 2 h. This result is quite different from the result obtained from the pure cyclohexanone solvent system discussed above. Grafted copolymers with a 40–60 fraction of grafting and gelatinous form were obtained. The free radical was difficult to collide with

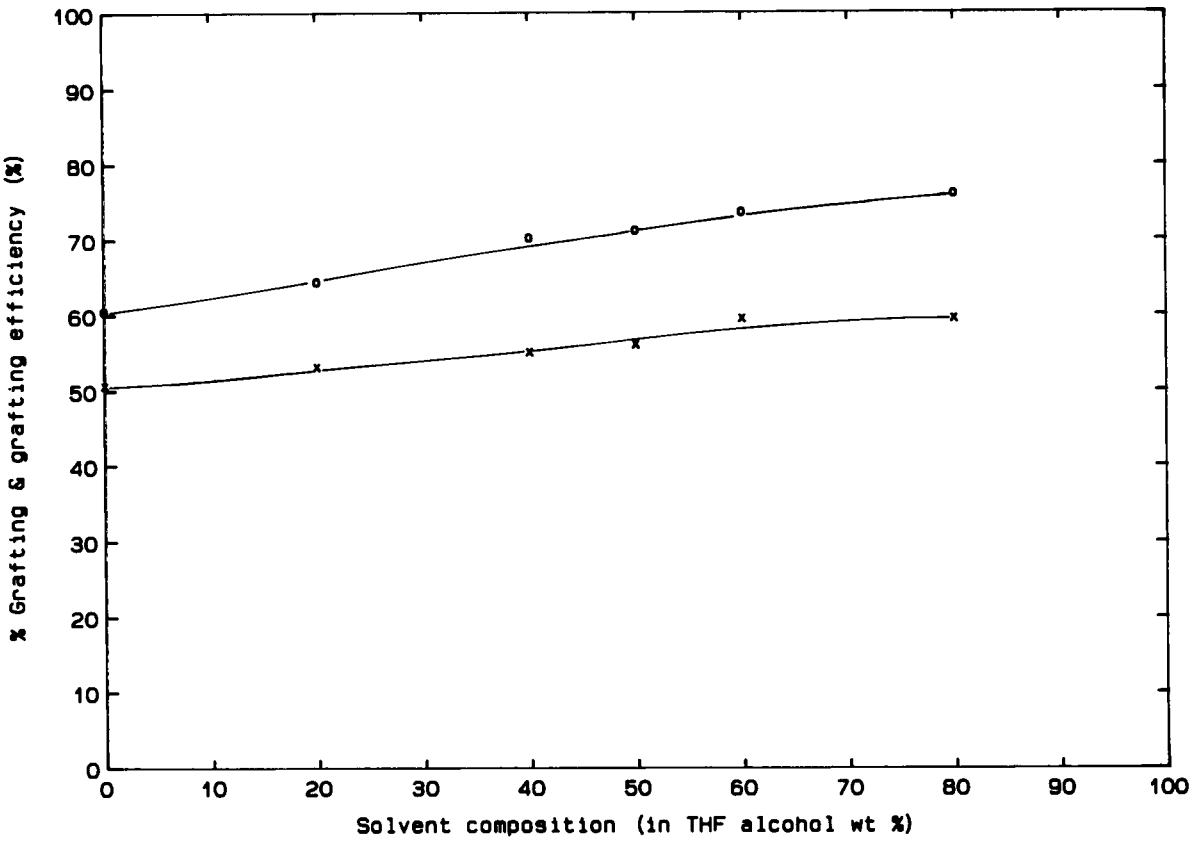


Figure 8 Effect of mixed solvent composition in grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. 10% NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC; reaction time: 3 h.

the grafted side chain during the latter period of duration. Restated, the chain transfer reaction of the grafted side chain would not occur; consequently, the high fraction of the grafting copolymer was maintained during the whole procedure. The conversion of the HEMA overall polymerization (C_p), grafting copolymerization (C_g), and homopolymerization (C_h) through the whole process are listed in Table III. The overall conversion of HEMA polymerization (C_p) is similar to the result obtained from the cyclohexanone grafting system (Table II). However, the conversion of the grafting copolymerization (C_g) and homopolymerization (C_h) increased with an increasing reaction time. The result demonstrated in Table III exhibits that the grafting copolymerization functioned in a major role in this system. The result of C_g, which gradually increased until a reaction duration of 6 h, indicated that the active sites on DHPVC were stepwise consumed.

Effect of DHPVC Concentration in Cyclohexanone

The fraction of grafting and grafting efficiency for a half-amount of HEMA/DHPVC (2.5 g DHPVC) are indicated from the above discussion to have become highly elevated (40–60%). Confirming those effects of DHPVC concentrations in cyclohexanone on the fraction of grafting or grafting efficiency therefore becomes important. The influence of various DHPVC concentrations (30–150 g/L solvent) on the fraction of grafting and grafting efficiency of the HEMA monomer was conducted. Those results are illustrated in Figure 10. A maximum fraction of grafting in the concentration of 75 g DHPVC/L cyclohexanone is indicated from the results in Figure 10. In a more dilute solution (< 75 g DHPVC/L solvent), the grafting increased with the DHPVC concentration increase. However, this grafting steeply decreased when the DHPVC concentration

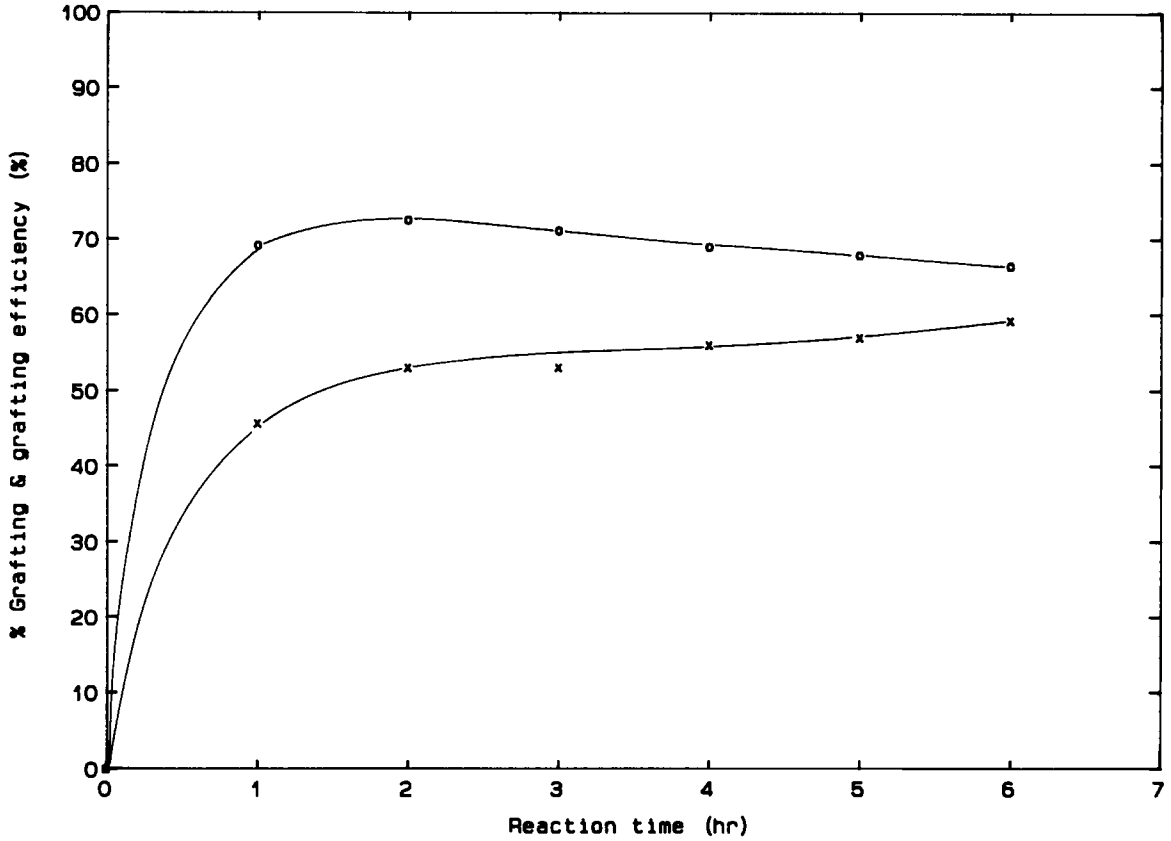


Figure 9 Effect of reaction time in the mixed-solvent grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. 10% NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC; solvent: cyclohexanone/tetrahydrofurfuryl alcohol, 50/50 wt %.

was more than 75 g/L. The result can also be examined from the conversion of HEMA listed in Table IV for overall polymerization (C_p), grafting copolymerization (C_g), and homopolymerization (C_h) in various concentrations of DHPVC. The solution becomes more viscous while the DHPVC concen-

Table III HEMA Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Mixed Solvent[b]

Time (h)	C_p (%)	C_g (%)	C_h (%)
1	62.78	47.51	15.27
2	71.82	54.25	17.57
3	85.08	59.63	25.45
4	92.22	63.98	28.24
5	98.02	66.14	31.88
6	99.21	66.36	32.85

[a] Ten percent NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC.

Table IV HEMA Conversion of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Cyclohexanone[a]

DHPVC Concn (g/L)	C_p (%)	C_g (%)	C_h (%)
30	60.30	6.39	53.91
50	79.04	47.82	31.22
70	84.60	70.89	13.71
100	85.58	5.96	79.62
120	88.89	3.94	84.95
150	90.48	2.58	87.90

[a] Ten percent NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC; reaction time: 3 h.

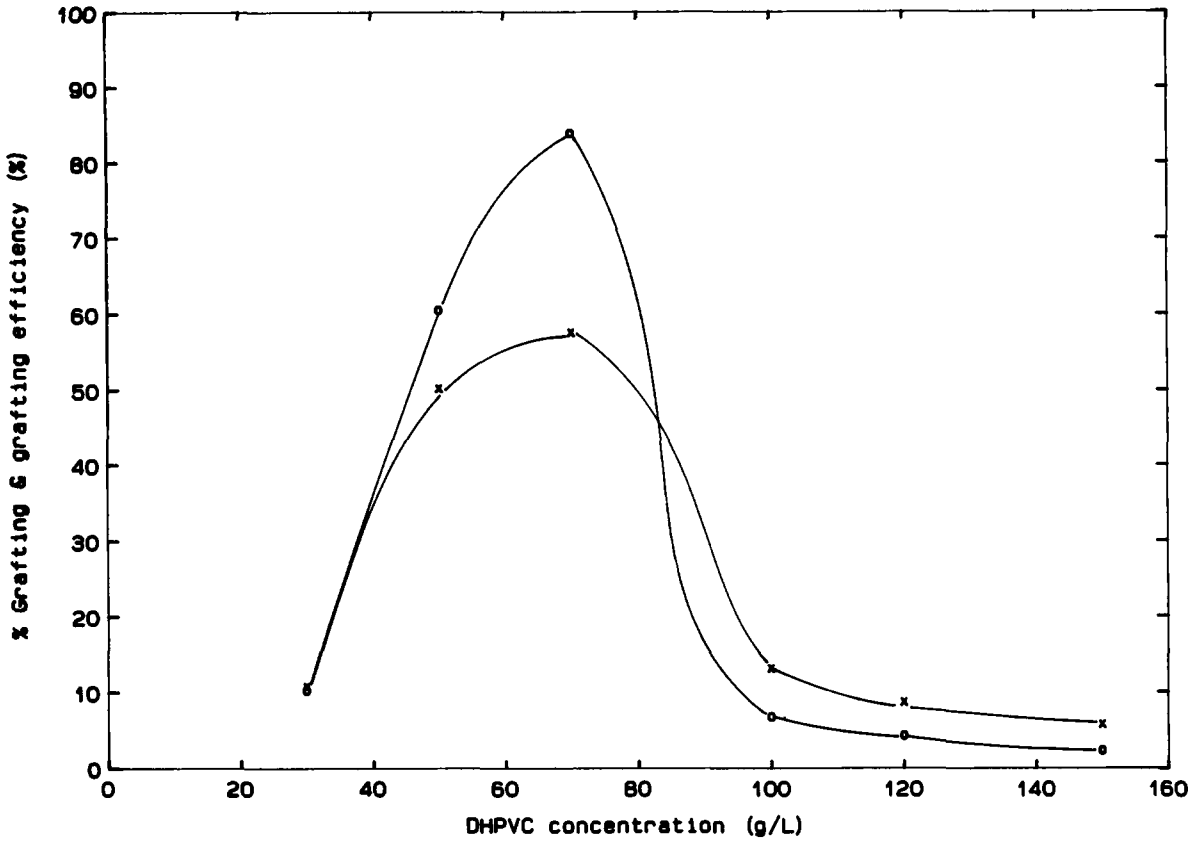


Figure 10 Effect of reaction agent concentration in the grafting reaction on the (x) fraction of grafting and (O) grafting efficiency. 10% NaOH-treated DHPVC; HEMA concentration 1.5×10^{-2} mol/g DHPVC; reaction time: 3 h; solvent: cyclohexanone.

tration was increased, as observed while the reaction proceeded. The viscous solution transformed into a turbid state when the reaction proceeded for 1 h. This phenomenon indicated that the polymer of HEMA was not dissoluble in cyclohexanone; additionally, phase separation and a heterogeneous system were formed. The combination of HEMA radicals was formed more easily in this situation. A large amount of HEMA homopolymer was formed and, consequently, decreased the fraction of grafting. Appropriately controlling the DHPVC concentration becomes, consequently, important for raising the fraction of grafting.

CONCLUSION

Grafting a hydrophillic monomer such as 2-hydroxyethyl methacrylate (HEMA) was confirmed in this present work to be capable of being successfully grafted onto dehydrochlorinated PVC (DHPVC) via chemical initiation. This grafting was accomplished by the reaction in a homogeneous system. Various reaction situations that affected the grafting copolymerization were examined. An extraordinary effect of reaction time in pure solvent was determined and a large percentage of grafting in mixed solvent was obtained. The major factor related to the DHPVC concentration of the grafting reaction was found. The applications of HEMA-grafted copolymer will be explored in our future research efforts.

REFERENCES

1. V. K. Krishnan and A. J. Krishnan, *Biomaterials,* **12,** 489 (1991).
2. E. P. Goldberg and A. Vahiaoui, U.S. Pat. 5,094,876.
3. J. Singh, A. R. Ray, J. P. Singhal, and Harpal Singh, *Biomaterials,* **11,** 473 (1990).

4. F. Vigo and C. Uliana, *J. Appl. Polym. Sci.*, **35,** 1893 (1988).
5. F. Vigo and C. Uliana, *J. Appl. Polym. Sci.*, **38,** 1197 (1989).
6. S. Sankholkar and P. C. Deb, *J. Appl. Polym. Sci.*, **39,** 1681 (1990).
7. J. Y. Lai, M. H. Chen, and K. Y. Hsu, *J. Appl. Polym. Sci.*, **46,** 489 (1992).
8. J. Y. Lai, T. C. Chang, Z. J. Wu, and T. S. Hsien, *J. Appl. Polym. Sci.*, **32,** 4709 (1986).
9. A. Jong, T. C. Chang, and J. Y. Lai, *J. Appl. Polym. Sci.*, **36,** 87 (1988).
10. S. G. Joshi and B. D. Kulkarni, *Angew. Makromol. Chem.*, **161,** 135 (1988).
11. N. Okumura, K. Kitaide, and K. Yamaguchi, *Kobunshi Ronbunshu,* **47**(3), 223 (1990).
12. N. Inoue, M. Okamura, S. Segay, and S. Watanabe, *Kobunshi Ronbunshu,* **45**(8), (1988).
13. P. Chosh, A. S. Bhattacharyya, and S. Maitra, *Angew. Makromol. Chem.*, **162,** 135 (1988).
14. A. K. Mukherjee and Achla Gupta, *J. Appl. Polym. Sci.*, **28,** 1245 (1983).
15. A. Al-mobasher, S. Attari, H. Pasch, K. F. Shuhaibar, and F. A. Rasoul, *Polym. Bull.*, **26,** 39 (1991).
16. K. K. Sharma and I. K. Varma, *J. Appl. Polym. Sci.*, **25,** 1079 (1980).
17. U. K. Saroop, K. K. Sharma, Madhumita Saroop, K. K. Jain, Ashok Misra, and S. N. Maiti, *Eur. Polym. J.*, **24**(7), 689 (1988).
18. El Sayed A. Hegazy, A. R. Ebaid, S. A. EL-Sharabasy, A. M. Mousa, and A. Y. Hassan, *J. Appl. Polym. Sci.*, **41,** 2941 (1990).
19. J. C. Gressier, *J. Macromol. Sci. Chem.*, **A23**(11), 1263 (1986).
20. W. F. Lee and C. C. Lai, in *Proceedings of the 16th ROC Polymer Symposium,* 1993, Vol. 9, No. 1, p. 225.

Received July 15, 1993
Accepted September 15, 1993