Graft Copolymerization of *N*-Isopropylacrylamide onto Poly(vinyl chloride)

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ABSTRACT: Poly(vinyl chloride) (PVC) was dehydrochlorinated in alkali solution and then grafted with *N*-isopropylacrylamide (NIPAM) using benzoyl peroxide as an initiator under a nitrogen atmosphere. The results show that grafting of NIPAM onto dehydrochlorinated PVC (DHPVC) by means of chemical initiation is easily performed. The influence of various reaction conditions such as NIPAM concentration, reaction time, initiator concentration, and PVC content on the grafting copolymerization was investigated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1234–1241, 1999

INTRODUCTION

The grafting copolymerization of vinyl monomers such as styrene and acrylates onto poly(vinyl chloride) has been studied extensively.[1–17] Graft methods that commonly used dehydrochlorination or γ-irradiation have been reported previously.[1–22] Hydrophilic monomer grafting was investigated by several scholars.[1–6,18–20] For example, Krishan and Krishan, Goldberg and Vahiaoui, and Singh and colleagues, respectively, investigated the grafting of *N*-(vinyl pyrrolidine), 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] Lai and colleagues also studied HEMA and other vinyl monomers grafted onto nylon 4 membrane.[18–20]

We have successfully grafted functional monomers such as HEMA[21] and glycidyl methacrylate (GMA)[22] onto PVC using benzoyl peroxide as a free radical initiator under a nitrogen atmosphere in previous studies. However, the graft copolymerization of thermoreversible monomers such as *N*-isopropylacrylamide (NIPAM) onto poly(vinyl chloride) was not found. Hence, the further investigation of the grafting of NIPAM onto PVC in a homogeneous procedure is the aim of this article. The effect of NIPAM concentration, reaction time, initiator concentration, and PVC content on the grafting percentage is investigated.

EXPERIMENTAL

Materials

PVC resin (S-70, DP = 1070) was supplied by Formosa Plastic Co. (Taiwan). *N*-Isopropylacrylamide (NIPAM) monomer was supplied by TCI (Japan). Benzoyl peroxide (BPO) was recrystallized by dissolving in chloroform at room temperature and then precipitated by methanol. Tetrahydrofuran (THF), *n*-hexane, cyclohexanone, and methanol were used as received.

Dehydrochlorination of PVC (DHPVC)[21,22]

A weighed quantity of PVC resin and 10 times its amount of 10% NaOH solution by mass were fed

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into a round-bottom flask fitted with a reflux condenser. 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).

PVC-*g*-NIPAM Grafted Copolymerization and Separation

A typical graft copolymerization of DHPVC with NIPAM is shown in Scheme 1. First, DHPVC (1 g) and solvent (10 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 80°C was reached, NIPAM monomer (a known amount containing BPO) was added with continuous stirring at this condition. The reaction was carried out for predetermined periods. The mixture was then cooled and poured into an excess of 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*-NIPAM and poly(NIPAM). Poly (NIPAM) was removed by a soxhlet extractor with methanol as a solvent. The remaining solid PVC-*g*-NIPAM was dried under vacuum and weighed.

Estimation of Grafting Parameters by Gravimetry

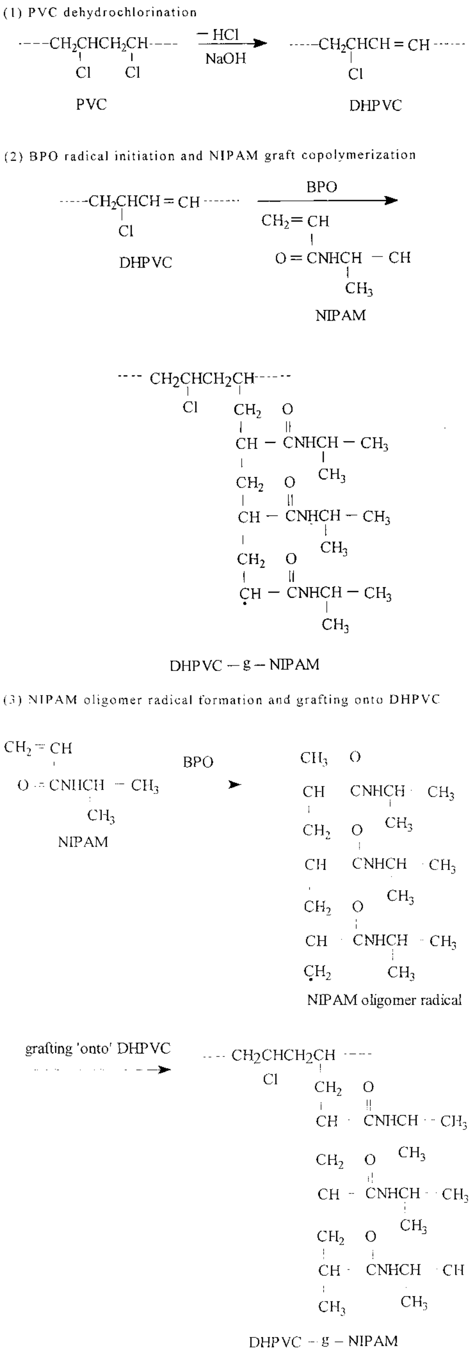
The grafting parameters were estimated from the mass of the sample before and after grafting. The percentage of grafting and the grafting efficiency were calculated according to the following relationships:

$$\text{NIPAM \% grafting} = \frac{\text{mass of NIPAM in PVC-}g\text{-NIPAM}}{\text{mass of grafted copolymer}} \times 100\% \qquad (1)$$

$$\text{Grafting efficiency} = \frac{\text{mass of NIPAM in PVC-}g\text{-NIPAM}}{\text{mass of NIPAM in PVC-}g\text{-NIPAM} + \text{mass of poly(NIPAM) homopolymer}} \times 100\% \qquad (2)$$

Characterization Techniques

IR spectra of solvent-cast films were measured on a spectrophotometer (Jasco FT/IR-300E) in the range 400 to 4000 cm^{-1}. Glass transition temperature (T_g) was determined by using a Du Pont 2000 differential scanning calorimeter (DSC). The sample was 8 mg of dried film. All samples were heated up to 150°C at heating rates of 20°C/min, and kept 90 s at that temperature to remove the



Scheme 1

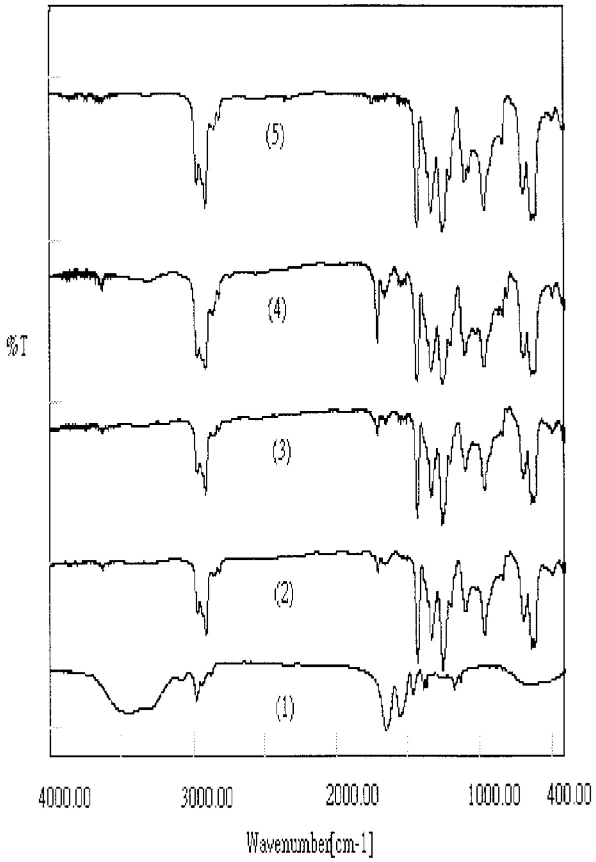


Figure 1. IR spectra of PVC, poly(NIPAM), and various fractions of grafted PVC-*g*-NIPAM: (1) poly(NIPAM); (2) 8% grafted; (3) 16% grafted; (4) 21% grafted; and (5) pure PVC.

traces of solvent, then quenched to −30°C, and kept at that temperature for 5 min, then reheated to 150°C at a heating rate of 20°C/min. This procedure used was first scan, repeated once. The T_g values adopted in this study were second-scan values.

RESULTS AND DISCUSSION

Characterization of Graft Copolymer

The use of IR spectroscopy is a well-known method to identify functional groups and to make quantitative analysis. The IR spectra of PVC, poly(NIPAM), and the graft copolymers are exhibited in Figure 1. The appearance of a new peak in the grafted sample at 1732 cm^{-1} indicates the addition of the carbonyl group of NIPAM. The transmittance corresponding to the intensity ratio of $\lambda_{C=O}$ (1732 cm^{-1})/λ_{C-Cl} (636 cm^{-1}) was calculated by the shoulder method and then a quantitative assessment was made to establish a relationship between the intensity ratio and percentage of grafting. The result is shown in Figure 2. The percentage of grafting for NIPAM grafted onto PVC increased linearly with an increase of the intensity ratio.

DSC Measurement (T_g Test)

The DSC curves for PVC, various PVC-*g*-NIPAM graft copolymers and poly(NIPAM) are shown in Figure 3. The glass transition temperatures (T_g) adopted from Figure 3 are demonstrated in Table I. The T_g of poly(NIPAM) was 408 K larger than that of PVC and the T_g of grafted copolymers increased with an increase of the percentage of NIPAM grafting. The T_g values shown in Table I (as calculated by Fox equation:

$$\frac{1}{T_g} = \frac{X_1}{T_{g1}} + \frac{X_2}{T_{g2}} \qquad (3)$$

where X_i is the weight fraction) approximately coincide with those analyzed by DSC. The data shown in Table I for the PVC-*g*-NIPAM system also exhibit only one T_g in various compositions. The range of T_g for grafted polymer is approxi-

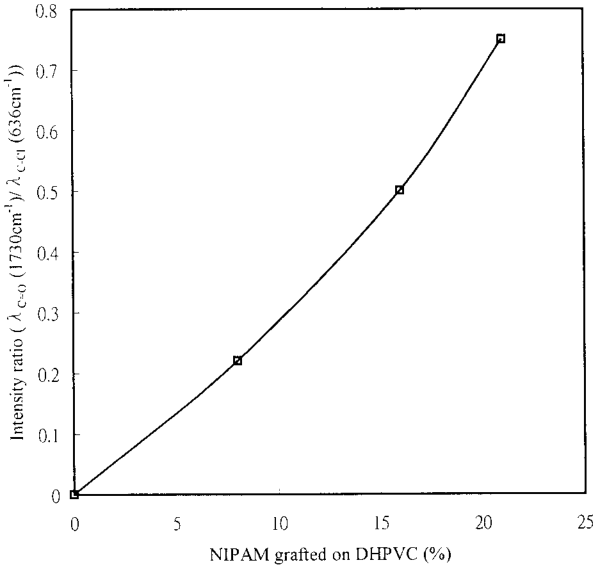


Figure 2. Fraction of grafting of NIPAM grafted onto PVC versus intensity ratio $\lambda_{C=O}$ (1730 cm^{-1})/λ_{C-Cl} (636 cm^{-1}) from IR spectra.

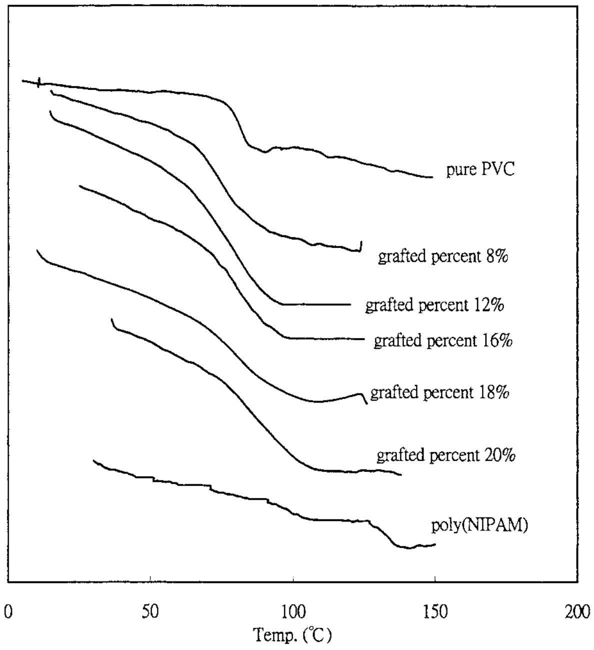


Figure 3. The DSC curves for PVC-*g*-NIPAM polymer.

mately 354 to 365 K. The single value of T_g of each grafted copolymer provided the evidence for complete separation of the copolymer mixture, that is, the material is a grafted product with chemical bonding, not a physical blend.

Effect of the NIPAM Monomer Concentration on the Grafting Percentage

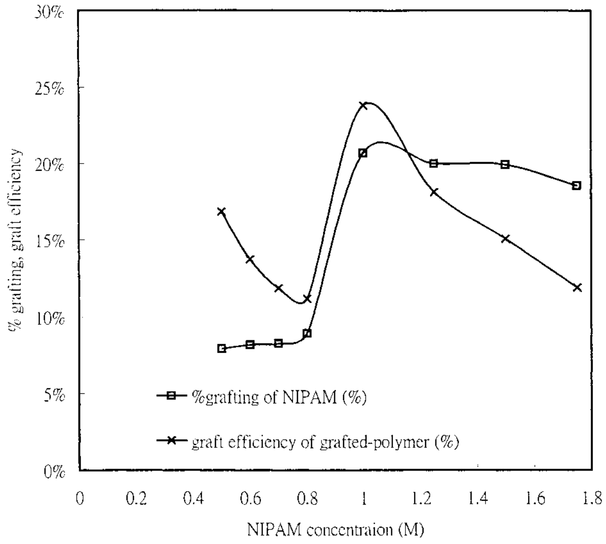


Figure 4. Effect of NIPAM concentration in grafting reaction on the grafting percentage and graft efficiency (PVC = 1 g, BPO = 1.13 × 10^{-2} mol, cyclohexanone =10ml, reaction time = 3 h).

The effect of the concentration of NIPAM in the range of approximately 0.5 to 1.75*M*/g DHPVC on conversion, graft efficiency, and grafting percentage, respectively, is shown in Figure 4 and Table II. The percentage of grafting of NIPAM increases gradually with the increase of monomer concentration of NIPAM from 0 to 1*M*. The percentage of grafting is 7.9% when the NIPAM concentration is 0.5*M*. Furthermore, it reaches a maximum value 20.7% when the NIPAM concentration increases to 1*M*. Beyond this concentration, the percentage of grafting keeps approximately constant. This result is similar to outcomes reported by Saroop and coworkers.[14] and our previous studies.[21,22] This is because the grafted chains generally grow until the active sites are occupied com-

Table I The Glass Transition Temperatures of PVC, PVC-*g*-NIPAM, and Poly(NIPAM)

Sample	NIPAM (%)	T_g (K)	$T_{g\,(\mathrm{Fox})}$ (K)
Pure PVC	0	354	354
PVC-*g*-NIPAM	8	354	356
PVC-*g*-NIPAM	12	355	358
PVC-*g*-NIPAM	16	358	359
PVC-*g*-NIPAM	18	363	360
PVC-*g*-NIPAM	20	365	361
Poly(NIPAM)	100	408	408

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

NIPAM Concentration (M)	C_p (%)	C_g (%)	C_h (%)
0.5	91.7	15.2	76.5
0.6	97.2	13.1	84.1
0.7	97.5	11.4	86.1
0.8	98.5	10.8	87.6
1.0	98.3	23.1	75.3
1.25	99.0	17.7	81.3
1.5	98.9	14.7	84.3
1.75	98.4	11.5	86.9

[a] Reaction time: 3 h; DHPVC: 1 g; cyclohexanone: 10 mL; initiator concentration: 11.3 × 10^{-3} mol.

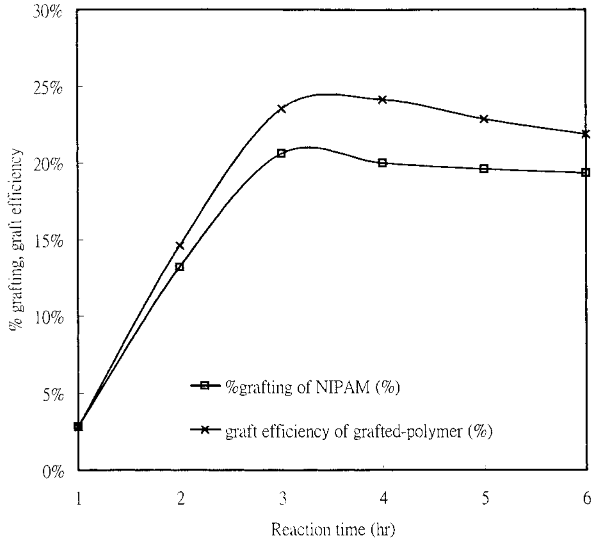


Figure 5. Effect of reaction time in grafting reaction on the grafting percentage and graft efficiency (PVC = 1 g, NIPAM = 1*M*, BPO = 1.13 × 10^{-2} mol, cyclohexanone =10 ml).

pletely and reach a maximum grafting percentage. Above this concentration (1*M*), the excess NIPAM monomer generated a large amount of poly(NIPAM) homopolymer (see Table II, C_h). This event results in reducing the graft efficiency. This result, shown in Table II for the conversion of NIPAM for overall polymerization (C_p), grafting copolymerization (C_g), and homopolymerization (C_h), can also be confirmed by the results in this polymerization condition. Table II also shows that C_p increases with increase in NIPAM concentration.

Effect of Reaction Time

The effect of reaction time in the range 1 to 6 h on grafting percentage and graft efficiency of NIPAM grafting onto DHPVC is shown in Figure 5. The percentage of NIPAM grafting increased continuously with increasing reaction time from 0 to 3 h. The percentage of grafting was 2.6% when the reaction time was 1 h. Furthermore, it reached a maximum value of 20% when the reaction time increased to 3 h. Beyond 3 h, the percentage of grafting and the efficiency of grafting kept approximately constant. This meant that the grafted chains generally grow until the active sites are occupied completely and reach maximum grafting at the particular time, after which the grafting percentage and the graft efficiency increase no more. This result is quite different from the results obtained from HEMA grafted onto DHPVC,[21] but similar to the results obtained from GMA grafted onto PVC.

Effect of the Initiator Concentration

The effect of the concentration of initiator BPO on the grafting was studied in the range of approximately 0.25 to 1.75 × 10^{-2} mol/g NIPAM (see Fig. 6). The percentage of grafting and grafting efficiency increases with an increase in concentration of initiator from 0.25 to 1.13 × 10^{-2} mol/g NIPAM. This trend can be explained by the fact that the radical transfer to the monomer is more pronounced on increasing the BPO, which results in the increase in grafting. However, beyond the concentration of 1.13 × 10^{-2} mol/g NIPAM, the grafting efficiency and graft percentage decrease. This is due to the conversion of homopoly (NIPAM) increasing again over 1.13 × 10^{-2} mol/g NIPAM (see Table III). The C_p shown in Table III also indicated a higher value at initiator concentration of 1.13 × 10^{-2} mol/g NIPAM.

Effect of DHPVC Concentration on the Grafting

The influence of various concentrations of DHPVC (about 0.8 to 2.0 g/20 mL) in cyclohexanone on the percentage of grafting and grafting efficiency of

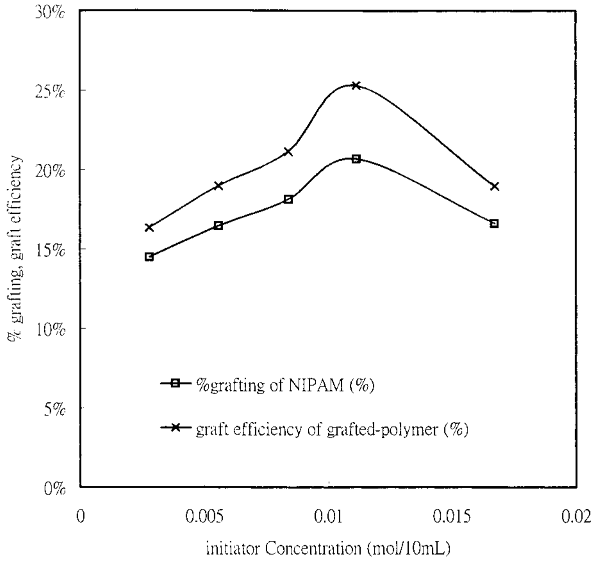


Figure 6. Effect of initiator concentration in grafting reaction on the grafting percentage and graft efficiency (PVC = 1 g, NIPAM = 1*M*, cyclohexanone = 10 ml).

Table III NIPAM Conversions of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Cyclohexanone[a]

Initiator Concentration (10^{-3} mol)	C_p (%)	C_g (%)	C_h (%)
2.8	97.2	15.0	82.2
5.6	97.2	17.4	79.8
8.4	98.2	19.6	78.6
11.3	96.3	23.1	73.2
16.7	98.2	17.6	80.7

[a] DHPVC: 1 g; NIPAM concentration: 1*M;* reaction time: 3 h.

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

DHPVC Concentration (g/20 mL)	C_p (%)	C_g (%)	C_h (%)
0.8	98.9	1.6	97.3
1.25	99.4	11.0	88.3
1.5	93.9	8.8	85.1
2.0	95.1	6.8	88.3

[a] NIPAM concentration: 1*M;* reaction time: 3 h; initiator concentration: 11.3 × 10^{-3} mol.

NIPAM monomer is shown in Figure 7. The result shown in Figure 7 indicates that the percentage of grafting and grafting efficiency of NIPAM monomer increases to a maximum value of 17%, whereas the concentration of the DHPVC increases to 1.25 g/20 mL. However, the percentages of grafting and grafting efficiency steeply decrease with an increase in DHPVC concentration. This result can also be seen from the conversion of NIPAM monomer as shown in Table IV for C_p, C_g, and C_h in various DHPVC concentrations. This event can be attributed to the solution's becoming more viscous when the DHPVC concentration was increased. A large amount of NIPAM homopolymer was then formed and decreased the percentage of grafting and grafting efficiency. This phenomenon was also observed in the previous study.[21]

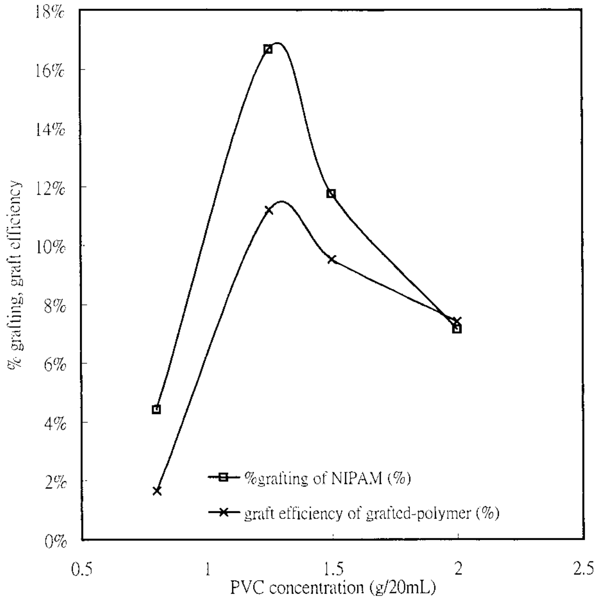


Figure 7. Effect of PVC concentraion in grafting reaction on the grafting percentage and graft efficiency (NIPAM = 1*M*, BPO = 1.13 × 10^{-2} mol, time = 3 h, cyclohexanone = 20 ml).

Effect of the Total Amount of Reaction Mixture

In Figure 4, the optimum grafting percentage was found at 1*M* NIPAM concentration per 1 g DHPVC in 10 mL cyclohexanone. The effect of the scale-up of this composition on the grafting percentage is investigated in this section.

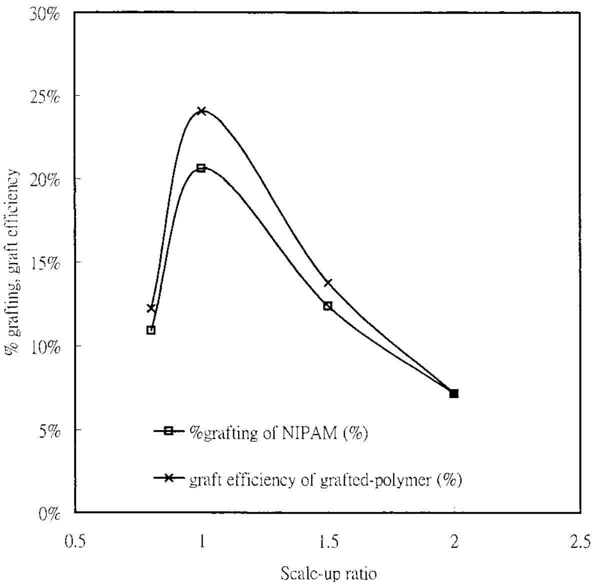


Figure 8. Effect of scale-up ratio in grafting reaction on the grafting percentage and graft efficiency (NIPAM = 1*M*, BPO = 1.13 × 10^{-2} mol, time = 3 h).

Table V NIPAM Conversions of Overall Polymerization (C_p), Grafting Copolymerization (C_g), and Homopolymerization (C_h) in Cyclohexanone[a]

NIPAM (g)	PVC (g)	Cyclohexanone (mL)	C_p (%)	C_g (%)	C_h (%)
0.9	0.8	8	93.0	10.8	82.2
1.1	1	10	97.5	23.0	74.6
1.7	1.5	15	94.9	12.5	82.4
2.3	2	20	95.1	6.8	88.3

[a] Reaction time: 3 h.

The effect of the scale-up ratio in the range of approximately 0.9 to 2 on the conversion and grafting percentage is shown in Figure 8 and Table V. The percentage of grafting of NIPAM increased continuously with increasing scale-up ratios from 0.8 to 1. The percentage of grafting was 11% when the scale-up ratio was 0.8. Furthermore, it reached a maximum value of 20.7% when the scale-up ratio increased to 1. Beyond this ratio, there was shown a dramatic effect: The percentage of grafting and the efficiency of grafting steeply reduced with increasing scale-up ratio. This result is similar to the result obtained from Figure 7. Hence, it can be deduced that the viscous effect observed in Figure 7 is the main effect in this scale-up copolymerization That is, the higher the viscosity in the graft copolymerization system, the more the formation of the homopolymer of (NIPAM). This result conforms to the conversion of poly(NIPAM) shown in Table V.

CONCLUSIONS

The grafting of NIPAM onto DHPVC by means of the chemical graft method has been successfully performed. Under reaction conditions chosen, the reaction time, monomer concentration, initiator concentration, and PVC contents for optimal grafting were determined.

Thus, (1) the percentage of grafting for NIPAM grafted onto DHPVC increases with the concentration of NIPAM monomer to a maximum value at 1*M*; (2) the percentage of grafting for NIPAM grafted onto DHPVC increases with the reaction time to a maximum value at 3 h; (3) the percentage of grafting for NIPAM grafted onto DHPVC increases with the content of initiator to a maximum value at 1.13×10^{-2} mol/g NIPAM, then it decreases appreciably with increasing initiator concentration; and (4) the percentage of grafting and grafting efficiency for NIPAM grafted onto DHPVC increases with the PVC content to a maximum value at 1 g PVC, then dramatically decreases with an increasing PVC amount in the reaction mixture.

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REFERENCES AND NOTES

1. Krishnan, V. K.; Krishnan, A. J. Biomaterials 1991, 12, 489.
2. Goldberg, E. P.; Vahiaoui, A. U.S. Pat. 5,094,876.
3. Singh, J.; Ray, A. R.; Singhal, J. P.; Singh, H. Biomaterials 1990, 11, 473.
4. Vigo, F.; Uliana, C. J Appl Polym Sci 1988, 35, 1893.
5. Vigo, F.; Uliana, C. J Appl Polym Sci 1989, 38, 1197.
6. Sankholkar, S.; Deb, P. C. J Appl Polym Sci 1990, 39, 1681.
7. Joshi, S. G.; Kulkarni, B. D. Angew Makromol Chem 1988, 161, 135.
8. Okumura, N.; Kitaide, K.; Yamaguchi, K. Kobunshi Ronbunshu 1990, 47(3), 223.
9. Inoue, N.; Okamura, M.; Segay, S.; Watanabe, S. Kobunshi Ronbunshu 1988, 45, 8.
10. Chosh, P.; Bhattacharyya, A. S.; Maitra, S. Angew Makromol Chem 1988, 162, 135.
11. Mukherjee, A. K.; Gupta, A. J Appl Polym Sci 1983, 28, 1245.
12. Al-mobasher, A.; Attari, S.; Pasch, H.; Shuhaibar, K. F.; Rasoul, F. A. Polymer Bull 1991, 26, 39.
13. Sharma, K. K.; Varma, I. K. J Appl Polym Sci 1980, 25, 1079.

14. Saroop, U. K.; Sharma, K. K.; Saroop, M.; Jain, K. K.; Misra, A.; Maiti, S. N. Eur Polym J 1988, 24(7), 689.
15. El-Sayed, A. H.; Ebaid, A. R.; El-Sharabasy, S. A.; Mousa, A. M.; Hassan, A. Y. J Appl Polym Sci 1990, 41, 2941.
16. Gressier, J. C. J Macromol Sci Chem 1986, A23(11), 1263.
17. Lee, W. F.; Lai, C. C. Proceedings of the 16th ROC Polymer Symposium, 1993, 9(1), 225.
18. Lai, J. Y.; Chen, M. H.; Hsu, K. Y. J Appl Polym Sci 1992, 46, 489.
19. Lai, J. Y.; Chang, T. C.; Wu, Z. J.; Hsien, T. S. J Appl Polym Sci 1986, 32, 4709.
20. Jong, A.; Chang, T. C.; Lai, J. Y. J Appl Polym Sci 1988, 36, 87.
21. Lee, W. F.; Lai, C. C. J Appl Polym Sci 1994, 51, 2175.
22. Lee, W. F.; C. Lai, C. C. J Appl Polym Sci 1995, 55, 1197.