Ultraviolet-Radiation Induced Graft-Copolymerization of Hydroxyethyl Methacrylate onto Cotton Cellulose

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SYNOPSIS

Two-hydroxyethyl methacrylate was grafted onto cotton cellulose using photoinitiation technique in the presence of the photoinitiator benzoin ethyl ether. Various parameters of the graft-copolymerization reaction, namely time, temperature, initiator, and monomer concentrations, were optimized using the grafting bath containing 10% methanol/acetone to dissolve the photoinitiator. The cotton sample, preswollen in sodium hydroxide, was subjected to grafting under optimized conditions. The preswollen samples showed higher graft add-on values at the equivalent monomer concentration. The moisture regain initially decreased at lower graft add-on levels and increased marginally with higher graft add-on. This behavior of the grafted substrate with respect to moisture regain has been explained.

INTRODUCTION

Cotton is a versatile, natural fiber possessing a number of useful textile properties. It is highly prone to various kinds of chemical modifications and, hence, has been subjected to a variety of reactions in the past. The graft-copolymerization, using vinyl monomers, is a reaction that modifies the fiber properties in accordance with the nature of the monomer used for grafting. Photo-induced grafting, using UV radiation, is among the most promising and practical methods of graft-copolymerization because of its simplicity.

Photoinduced graft-copolymerization of cellulose with the use of photoinitiators such as dyes,[1] metal ions,[2] hydrogen peroxide,[3,4] etc., has been reported. Ceric ion was found to accelerate UV-radiation induced photografting of methyl methacrylate onto cellulose.[5,6] Davis et al.[7] have reported photoinduced graft-copolymerization of styrene and methyl methacrylate onto cellulose by using alcohols as solvents in the presence of various photoinitiators. The effect of organic solvents on the swelling of cotton fiber for improved graft-copolymerization was studied by Kubota et al.[8] They reported that the swelling of fiber has a favorable effect on increasing the diffusion of the monomer inside the fiber causing increased graft add-on.

The photoinitiated graft-copolymerization of cotton yarn, using 2-hydroxyethyl methacrylate monomer and uranyl nitrate and ceric ammonium nitrate photoinitiators, has already been reported.[9]

In the present article, the results on photoinduced liquid phase grafting of 2-hydroxyethyl methacrylate monomer onto cotton yarn in the presence of an organic photoinitiator benzoin ethyl ether, using a high pressure mercury vapor lamp as a source of UV-radiation, have been communicated. The effect of the swelling of cotton cellulose on the graft add-on was also studied using the inorganic swelling agent, sodium hydroxide. The grafted samples were subjected to moisture regain and infrared spectral analysis.

EXPERIMENTAL

Materials

Substrate

Scoured and bleached 30s count cotton yarn was used as a cellulose sample.

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Chemicals

Two-hydroxyethyl methacrylate (HEMA), supplied by Aldrich Chemical Company Inc., was vacuum distilled to make it free from the inhibitors. Benzoin ethyl ether (BEE) was the photoinitiator used.

Swelling of Cotton Cellulose

The swollen sample of cotton was prepared by using 24% (w/w) sodium hydroxide at 20°C for 1 h, followed by water-washing and drying in air at room temperature. The degree of swelling of the swollen cotton fiber was measured by noting the percentage change in the diameter of the fiber on a Projection Microscope MP-3 PZO, Warazawa, Poland.

$$\text{Swelling, \%} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_1 = Diameter of the fiber before swelling, and W_2 = Diameter of the fiber after swelling.

Graft Copolymerization

The cotton cellulose sample to be grafted was weighed at 1 g and immersed in 100 mL of the grafting bath in a quartz conical flask. The grafting bath was made up of the monomer and the initiator dissolved in 10 : 90 methanol : water or acetone : water mixture. A Philips HPW 125 W mercury lamp was used as a source of UV radiation. The temperature range of 30°–60°C was used and the reaction temperature was controlled by using glycerine bath. The quartz flasks were irradiated for different time intervals varying from 1 to 6 h in an enclosed wooden chamber containing an UV lamp. After the completion of the grafting reaction, the sample was removed, washed with methanol, and was then extracted with a boiling methanol : water (50 : 50) mixture for 7 h each, three times, to remove the homopolymer formed. After each extraction, the sample was washed with methanol and then with water, followed by air-drying. The graft add-on and the graft yield were determined as shown in eqs. (2) and (3):

$$\text{Graft add-on, \%} = \frac{W_2 - W_1}{W_1} \times 100, \text{ and} \qquad (2)$$

$$\text{Graft yield, \%} = \frac{W_2 - W_1}{W_3} \times 100 \qquad (3)$$

where W_1 = Weight of the original sample, W_2 = Weight of the grafted sample, and W_3 = Weight of the monomer taken initially.

Moisture Regain

The moisture regain of control and grafted cotton was determined by oven-drying method.[10]

Infrared Spectral Analysis

Infrared spectra were recorded on Perkin Elmer 391 Infrared Spectrophotometer. Two milligrams of cut fiber sample were mixed with 198 mg of potassium bromide and pellet was prepared. Scanning was carried out from 4000 cm^{-1} (2.5 μ) to 650 cm^{-1} (15.4 μ) at a slow speed.

RESULTS AND DISCUSSION

Effect of Photoinitiator Concentration

Benzoin ethyl ether (BEE) is an organic photoinitiator insoluble in water and soluble in solvents such as methanol and acetone, while the monomer 2-hydroxyethyl methacrylate (HEMA) is miscible with water as well as methanol and acetone. Initial experiments conducted showed that the graft-copolymerization reaction does not take place in pure methanol or in acetone medium. Further, different proportions of solvent–water mixtures were used as grafting media and it was found that the 10 : 90 mixture could only be used for efficient grafting. Thus, BEE was first dissolved in 10 mL methanol/10 mL acetone and then was diluted with water to 100 mL.

The effect of BEE photoinitiator concentration on the grafting of HEMA onto cotton cellulose was studied by varying its concentration in the range of 0.10% (w/v) to 0.40% (w/v). Figure 1 shows the changes in the HEMA graft add-on with increase in the initiator concentration. The maximum graft add-on of 5.94% was obtained at 0.30% (w/v) BEE concentration in methanol : water grafting bath, whereas, 4.42% graft add-on was achieved at 0.25% (w/v) BEE in acetone : water grafting medium. Beyond these specific concentrations of the initiator, however, further increase brought about a decrease

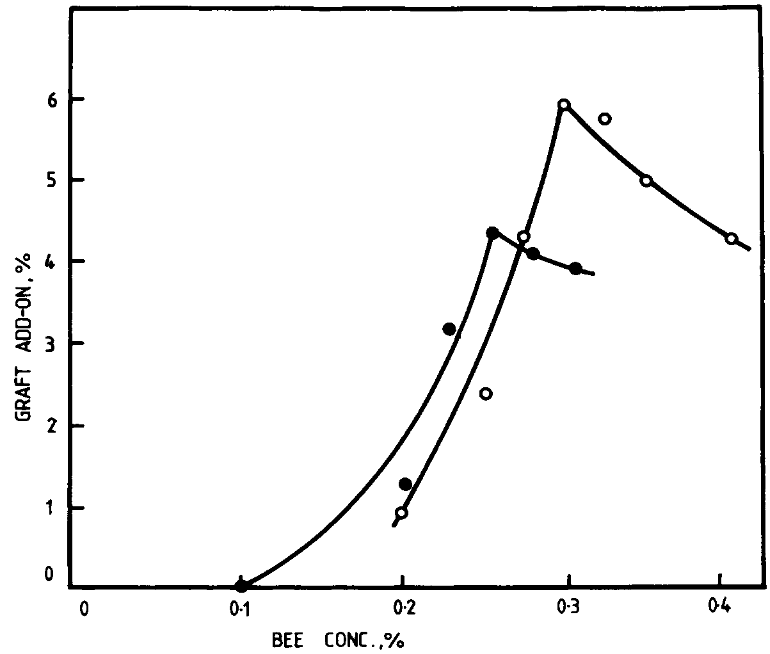

Figure 1 Relation between BEE concentration and graft add-on: (○) Methanol : water medium, (●) Acetone : water medium.

in the graft add-on values. In the presence of excess photoinitiator, it is likely that the growing polymer chains terminate rapidly. Cumberbirch et al.,[11] while grafting acrylic acid onto cellulose, observed a similar effect of the increased photoinitiator concentration.

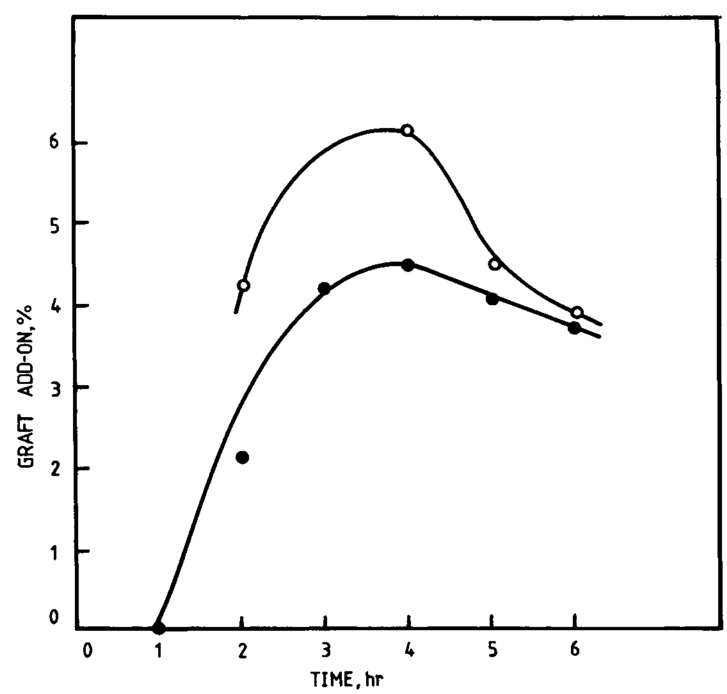

Figure 2 Relation between time of reaction and graft add-on: (○) Methanol : water medium, (●) Acetone : water medium.

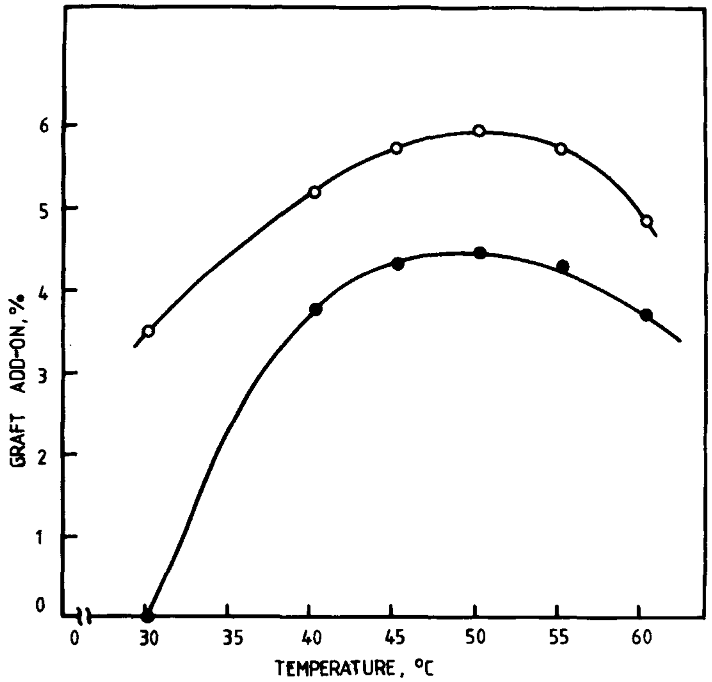

Figure 3 Relation between temperature of reaction and graft add-on: (○) Methanol : water medium, (●) Acetone : water medium.

Effect of Reaction Time

The effect of time of reaction on the graft add-on is shown in Figure 2. The HEMA graft add-on increased with time of grafting from 1 to 4 h, giving the values of 5.94% and 4.42%, respectively, in the grafting bath containing methanol : water and acetone : water mixtures. This would be due to the increasing extent of initiation and propagation of the graft-copolymerization reaction with time. Beyond 4 h, however, graft add-on was found to decrease progressively. The decrease in the graft add-on values was presumably due to the detrimental effect of UV radiation onto the grafted side chains of HEMA at longer irradiation times in the presence of the photoinitiator. Irradiation of the grafted cotton samples in the absence of initiator, however, did not have any effect on the graft add-on. Fouassier et al.[12] also observed similar behavior in case of methyl methacrylate grafting onto cellulose in the presence of benzophenone photoinitiator.

Effect of Reaction Temperature

Figure 3 shows the effect of reaction temperature on the graft add-on. The graft add-on increased with increasing temperature up to 50°C for both the grafting baths, beyond which, adverse effect on the graft add-on was observed. This was attributed to the increased extent of radical termination at higher temperature of reaction.

Effect of Monomer Concentration

The HEMA concentration was varied between the range of 0.15% (w/v) and 6.0% (w/v) to see the effect on graft add-on. Figure 4 shows that there is a significant increase in the graft add-on with increase in the monomer concentration, finally causing the leveling off of the grafting. The maximum graft yield was observed at 4% (w/v) HEMA concentration (Fig. 5), suggesting thereby that the utilization of the monomer is better at this concentration than that at any other concentration used. Although higher graft add-on values have been obtained beyond 4% (w/v) HEMA, there is correspondingly higher homopolymer formation also, which leads to the lowering of the graft yield at higher monomer concentration. Hence, 4% (w/v) HEMA concentration was thought to be optimum for obtaining reasonably high graft add-on with maximum utilization of the monomer. The infrared spectrum for

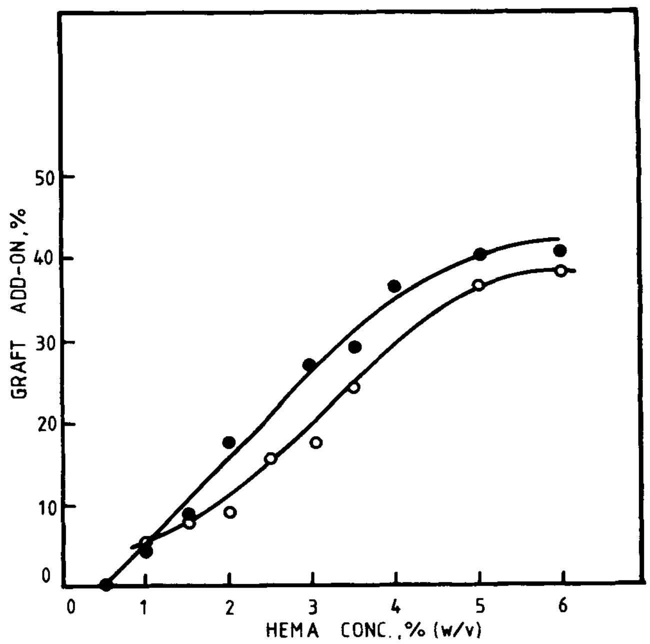

Figure 4 Relation between HEMA concentration and graft add-on: (○) Methanol : water medium, (●) Acetone : water medium.

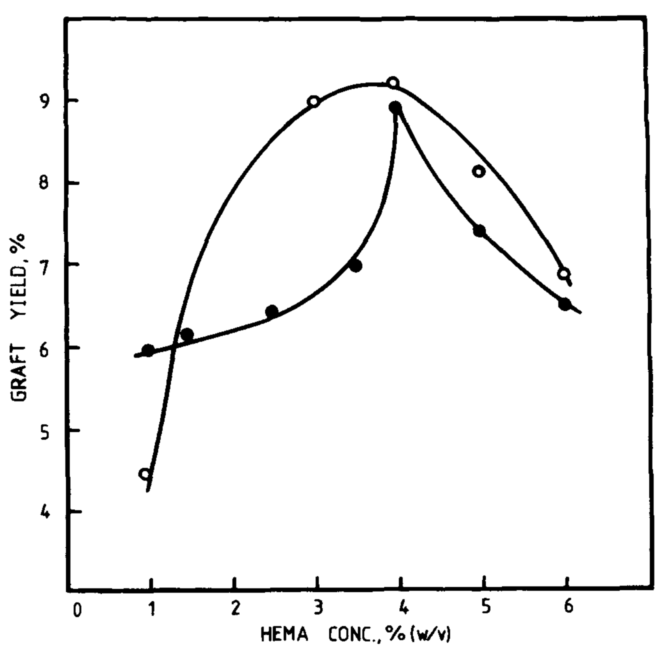

Figure 5 Relation between HEMA concentration and graft yield: (○) Methanol : water medium, (●) Acetone : water medium.

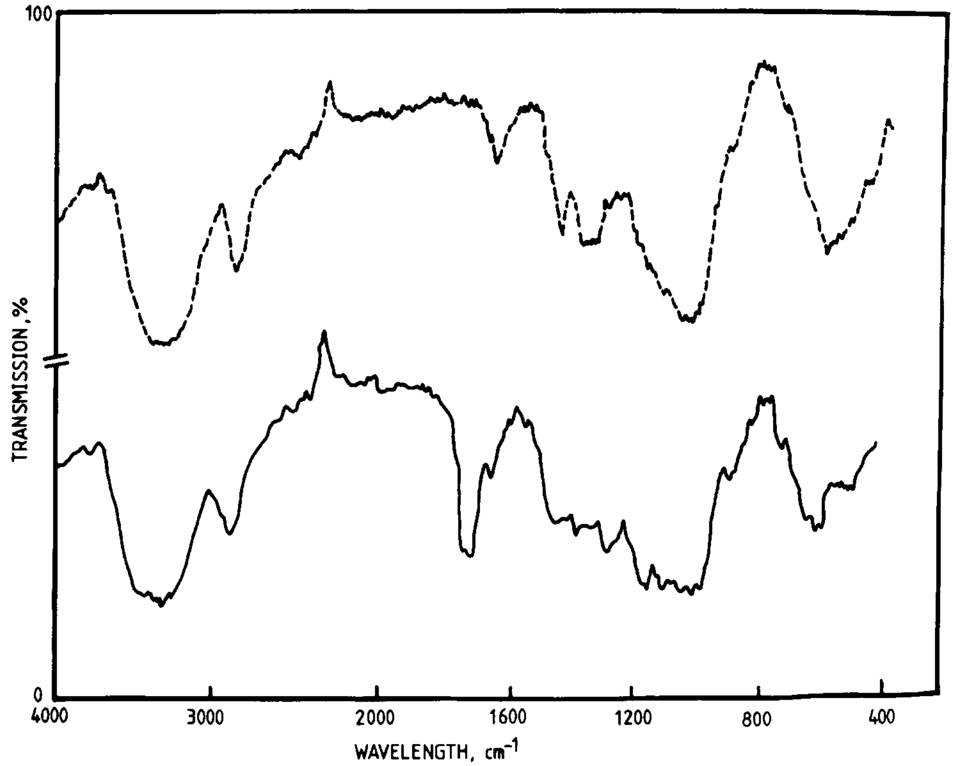

Figure 6 Infrared spectrum of samples: (——) control cotton, (- - -) HEMA-grafted cotton.

the grafted cotton has been given in Figure 6, which shows an additional peak at 1700 cm^{-1}, confirming the introduction of ester carbonyl groups belonging to the graft in the cellulose structure.

Effect of Swelling

The increase in the diameter of the fiber on swelling was taken as a measure of the extent of swelling. The diameter measurements of the fiber indicated about 30% increase in the diameter on swelling the substrate in sodium hydroxide. The grafting of HEMA onto swollen cotton was carried out under optimized conditions of time, temperature, and initiator concentration by varying the concentration of HEMA in the range of 1 to 4% (w/v). These results are presented in Table I, which indicate that the swollen cotton cellulose gives correspondingly higher graft add-on values than those for the unswollen substrate at each concentration of HEMA used. The higher graft add-on values in the case of swollen cotton were mainly attributed to the higher accessibility and greater reactivity of the swollen substrate as compared to the unswollen one. However, the effect of swelling on enhancement of graft add-on was less pronounced at the higher concentrations of HEMA.

Table I Effect of Swelling on Grafting of HEMA onto Cotton Cellulose

HEMA Concentration, % (w/v)	Cotton Sample	Graft Add-on, % Methanol : Water	Graft Add-on, % Acetone : Water
1	Unswollen	5.94	4.42
	NaOH-swollen	9.56	7.38
2	Unswollen	9.30	17.96
	NaOH-swollen	13.23	23.22
3	Unswollen	16.68	26.96
	NaOH-swollen	23.02	33.64
4	Unswollen	35.42	36.80
	NaOH-swollen	40.83	42.18

[a] Methanol : water = 10 : 90, 0.30% (w/v) BEE, 50°C, 4 h.
[b] Acetone : water = 10 : 90, 0.25% (w/v) BEE, 50°C, 4 h.

Table II Effect of Grafting of HEMA on Moisture Regain of Cotton Cellulose

	Methanol : Water				Acetone : Water			
	Unswollen		Swollen		Unswollen		Swollen	
HEMA Concentration, % (w/v)	Graft Add-on, %	M. R., %	Graft Add-on, %	M. R., %	Graft Add-on, %	M. R., %	Graft Add-on, %	M. R., %
0.0	0.00	6.13	0.00	9.18	0.00	6.13	0.00	9.18
1.0	5.94	5.43	9.56	8.58	4.42	5.50	7.38	8.54
2.0	9.30	5.54	13.23	8.60	17.96	5.60	25.22	8.67
3.0	16.68	5.60	23.03	8.83	26.96	5.67	33.64	8.72
4.0	35.42	5.73	40.83	8.80	36.80	5.74	42.18	8.80
5.0	36.76	5.74	—	—	40.68	5.79	—	—
6.0	38.56	5.76	—	—	41.04	5.80	—	—

Moisture Regain

The moisture regain values for the control cotton and those for the NaOH-swollen cotton samples were 6.13% and 9.18%, respectively. On grafting HEMA onto these samples, it was observed that initially, at low graft add-on levels, the moisture regain decreased markedly followed by a small steady rise with further increase in the graft add-on. These observations are shown in Table II. The measurement of the diameter of the swollen and the grafted cotton samples indicated further increase over that of the control swollen cotton.

It is well known that the amount of moisture absorbed by a substrate from atmosphere is dependent upon the physical factors, such as the atmospheric humidity and the accessible nature of the substrate. It is also related to the availability of the hydroxyl groups present in the cellulosic chains of cotton cellulose. Thus, swollen cotton has higher moisture regain as compared to that of unswollen cotton. Under identical physical factors, however, the presence of accessible —OH groups is the main criteria for the absorption of moisture by the fiber. When the cotton samples are grafted with HEMA, initially at low graft add-on levels up to 4.42% for unswollen grafted cotton, the moisture regain decreases as a result of the nonavailability of the cellulosic —OH groups for hydrogen bonding with the moisture, perhaps due to the steric hindrance caused by the bulky HEMA molecules.

After a graft add-on of 4.42%, there is a slight and gradual increase in the moisture regain. This may be solely attributed to the increased presence of new —OH groups due to grafted HEMA molecules onto the substrate. In such a case, the well known 1 : 1 relation between the available —OH groups from HEMA graft chains and the sorbed moisture molecules may be expected.[13] The nonabiding nature of the present system to the normally observed phenomenon may again be attributed to the hindrance caused by the HEMA grafted chains themselves due to their bulkiness. This may be likely, since only the —OH groups from the grafted chains near the surface of the fiber will be accessible to moisture, whereas those from the chains deep inside the structure will not be accessible, although there is slight lateral swelling observed in the fiber.

The calculations showed that the ratio of —OH due to HEMA to the sorbed moisture molecules was more than 15, which substantiates the postulation that all the —OH groups due to HEMA are also not available for moisture sorption. Thus, ultimately at a graft add-on of 41.04%, the moisture regain was found to be 5.80%, that is, almost that of the control sample.

CONCLUSION

The photoinitiation technique of graft-copolymerization provides an effective tool for modifying the physical as well as chemical properties of a backbone polymer. Since UV radiations are not strong enough, in order to enhance the graft add-on levels, preswelling of the substrate helps a lot without deteriorating the substrate properties. The effectiveness of the grafting technique is also dependent on the substrate–monomer–photoinitiator combination.

REFERENCES

1. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **3,** 54 (1960).
2. Y. Ogiwara and H. Kubota, *J. Appl. Polym. Sci.*, **16,** 337 (1972).
3. Y. Ogiwara and H. Kubota, *J. Appl. Polym. Sci.*, **14,** 3039 (1970).
4. S. Lenka and P. L. Nayak, *J. Appl. Polym. Sci.*, **27,** 3787 (1982).
5. Y. Ogiwara and H. Kubota, *J. Polym. Sci. A-1*, **6,** 3118 (1968).
6. Y. Ogiwara and H. Kubota, *J. Appl. Polym. Sci.*, **14,** 2610 (1970).
7. N. P. Davis and J. L. Garnett, *J. Polym. Sci.*, **C-55,** 287 (1976).
8. H. Kubota, Y. Murata, and Y. Ogiwara, *J. Polym. Sci. Polym. Chem. Ed.*, **11,** 485 (1973).
9. S. R. Shukla, G. V. Gopala Rao, and A. R. Athalye, *J. Appl. Polym. Sci.*, **42,** 2163 (1991).
10. L. Valentine, *Chem. Ind.*, 1279 (1956).
11. R. J. E. Cumberbirch and J. R. Holker, *J. Soc. Dyers Colour.*, **82,** 59 (1966).
12. J. P. Fouassier and R. Herdol, *Angew. Makromol. Chem.*, **86,** 123 (1980).
13. J. A. Barrie, *Diffusion in Polymers,* J. Crank and G. S. Park, Eds., Academic, London, 1968, p. 262.

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