Effect of Na-Light Radiation on the Optical Gap and Crystal Structure of AgNO₃-Diffused PVDF Sensor

A. TAWANSI,[1] A. H. ORABY,[1] E. AHMED,[2] E. M. ABDELRAZEK,[1] M. ABDELAZIZ[1]

[1] Department of Physics, Faculty of Science, Mansoura University, 35516, Egypt

[2] Department of Mathematics, Faculty of Science, Mansoura University, 35516, Egypt

ABSTRACT: A casting method was used to prepare polyvinylidene fluoride (PVDF) and 1 wt % $MnCl_2$-filled PVDF films. $AgNO_3$ was allowed to diffuse through the filled films. The 3 types of the prepared films were irradiated by Na light with various doses. The post-irradiation and relaxation effects were investigated using ultraviolet–visible spectroscopy, X-ray analysis, and optical microscopy. The results were interpreted on the bases of a theoretical model previously suggested for a build-up and decay of radiation-induced conductivity associated with the transition of charge carriers in the presence of a uniform trap distribution. Various structures were proposed for the diffused $AgNO_3$ before and after irradiation. It was found that the induced change in optical gap, due to 5-min irradiation time for the $AgNO_3$ diffused films, exhibits no relaxation phenomenon. Accordingly, this film can be used in photorecording applications. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1759–1767, 1998

Key words: $MnCl_2$-filled PVDF; $AgNO_3$ diffusion; Na-light irradiation; optical gap; X-ray diffraction

INTRODUCTION

Besides its several interesting physical properties, which are very useful in technical applications,[1] PVDF is known as a photosensitive material.[2] The problem of the bulk photoelectric effect modelling in ferroelectric polymeric films was treated on strictly formal grounds in Balachandran et al.[3] According to this general treatment, a mechanism explaining the charge transfer phenomena inside the polymeric films was developed. This enables one to determine the factors affecting the photoelectric phenomena and to enhance this effect. The experimental results of the same work[3] for PVDF films filled with transition metal halides fulfilled the findings of the developed model.

Irradiation-induced structural changes in polymers are due mainly to chemical transformations originating from the formation of radicals ions via a selective bond cleavage.[4] In this type of cleavage, even though the energy available largely exceeds the amount required to cleave any bond, the bonds are not broken at random.

PVDF, as a multiphase material, exhibits certain physical properties resulting from crystal–amorphous interfacial effects.[5–9]

Recently,[10] we have investigated the effect of local structure of $MnCl_2$-filled PVDF films on their optical, electrical, electron spin resonance, and magnetic properties. The filling level (W) dependence of the local structure of $MnCl_2$ through the PVDF matrix was explored. The presence of α- and β-PVDF crystalline phases were detected by X-ray diffraction, and it was confirmed by the infrared (IR) absorption spectra. A significant head-to-head content ($\sim$ 12%) was implied by IR analysis. An interchain one-dimensional interpo-

laron hopping mechanism was assumed to proceed. The calculated charge carrier hopping distance was in the range of 6.5–9.7 nm. The temperature dependence of the dc magnetic susceptibility exhibited a Curie–Weiss behavior. Positive values of the paramagnetic Curie temperature (θp) for $W \leq 14.5\%$ indicated the presence of ferromagnetic interactions, while negative θp obtained for $W > 14.5\%$ suggested an antiferromagnetic interaction, at lower temperatures.

It could be implied from[10] that 1% $MnCl_2$ filling was characterized by the following.

1. The highest degree of crystallinity of PVDF.
2. Clear, 6 hyperfine lines (due to isolated Mn^{2+} in ionomer) superimposed on a Lorentzian signal (indicating Mn^{2+}–Mn^{2+} exchange interaction of the aggrigated Mn^{2+}. The low value of peak-to-peak separation and the asymmetry value of ~ 1 of the Lorentzian signal revealed that Mn^{2+} exhibits the most symmetric local distribution in the PVDF matrix. Accordingly, filling PVDF with 1% $MnCl_2$ may lead to a less-compact matrix containing a main symmetric distribution of Mn^{2+} (around the PVDF chains). This is a suitable pattern for an easier and homogeneous $AgNO_3$ diffusion, desired for the present work.

The present work was devoted to investigate the influence of Na-light radiation on the optical energy gap and the crystal structure of the following films: (1) PVDF, (2) 1% $MnCl_2$-filled PVDF, and (3) $AgNO_3$-diffused and 1% $MnCl_2$-filled PVDF. The post-irradiation effect (PIE) and relaxation phenomena (RP) were explored for various exposure times.

EXPERIMENTAL

The studied PVDF films were prepared by a casting method. PVDF powder (SOLEF 1008) was dissolved in dimethylformamide (DMF). $MnCl_2$ was also dissolved in DMF. The solution of $MnCl_2$ was added to dissolved polymer with a suitable viscosity. The mixture was cast to a glass dish and kept in a dry atmosphere at 50°C for 2 weeks to insure the removing of solvent traces. The thickness of the obtained films was of the range of 0.1 to 0.2 mm. The samples were classified into 3 groups: pure PVDF films, 1 (wt %) $MnCl_2$-filled PVDF films, and 1 (wt %) $MnCl_2$-filled and

$AgNO_3$-diffused PVDF films. Hereafter, the 3 groups will be denoted by G1, G2, and G3, respectively.

$AgNO_3$ diffusion was carried out by floating films of G2 group on a surface of 10% $AgNO_3$ water solution, kept in the dark, for 48 h at 50°C. Thus, the diffusion process was allowed to proceed through 1 surface of the polymeric film. Then the films were transferred to a dry and dark place and kept there for 1 week. Such samples belong to G3.

Ultraviolet–visible (UV–vis) absorption spectra were measured in the wavelength region of 200 to 800 nm using a spectrometer (Perkin–Elmer UV–vis). The X-ray diffraction (XRD) scans were obtained using a Seimens type F diffractometer with $CuK\alpha$ radiation and a LiF monochromator. The optical photographs were carried out using Olympus microscope BH2 PM-10AK (automatic camera).

The light irradiation was done using a Sodium lamp type (Phillips G/5812 SON) of monochromatic wavelength of 5812 A°. The thermal effects of the Na lamp were compensated by regulating the sample temperature to be fixed around 298 ± 1 K. The PIE and the RP were investigated. The PIE was detected by carrying out the optical absorption spectra (OAS) 1 min after switching off the Na lamp, while the RP was explored by measuring the OAS periodically, with a periodic time of 4 days.

RESULTS AND DISCUSSION

Optical Absorption

The optical absorption spectra in the UV–vis region (200−800 nm) were measured for all of the studied films. The absorption coefficient $\alpha(v)$ at various frequency v values was calculated using the following equation.[11]

$$\alpha(v) = \ln[t_1(v)/t_2(v)]/(d_1 - d_2) \qquad (1)$$

where t_1 and t_2 are the transmittances of 2 films (of the same structure) with thicknesses d_1 and d_2. Plotting $(\alpha hv)^{1/2}$ as a function of the photon energy hv (where h is Planck's constant), we obtain curves exhibiting linear portions, as shown in Figure 1. Each linear portion characterizes an optical energy gap Eg, according to Davis and Mott formula,[12] as follows:

$$\alpha(v) = B(hv - Eg)^2/hv \qquad (2)$$

Figure 1 The photon energy dependence $(\alpha h v)^{1/2}$ for G1 films at various irradiation times (in min): (*) zero, ($\triangle$) 5, ($\bullet$) 10, ($\blacksquare$) 15, and ($\bigcirc$) 20.

where B is a constant. The optical gap for each of the studied samples was obtained using the foregoing procedure. Figure 2 depicts that the PIE on the optical gap (Eg_1 and Eg_2), of G1 and G2 samples (for various exposure times, t) can be fitted by eqs. (3) and (4), respectively.

Figure 2 The post-irradiation effect on the optical gaps ($\bullet$) $Eg1$ for G1 and ($\triangle$) $Eg2$, for G2 at various exposure times.

Figure 3 The relaxation phenomena of the normalized optical gaps (*) Egn_1 and (●) Egn_2 for G1 and G2 films, respectively.

$$Eg_1 = 1.2457 + 0.0057\, t - 0.0023\, t^2 \quad (3)$$

$$Eg_2 = 1.1875 + 0.0355\, t - 0.0025\, t^2 \quad (4)$$

Figure 3 shows the RP of the normalized optical gaps Egn_1 and Egn_2 of G1 and G2 samples, respectively, where $t = 5$ min. The normalized optical gap is defined as

$$Egni = (Eg_0 i - Egi)/Eg_0 i \quad (5)$$

where i is 1 and 2 (for G1 and G2 samples, respectively), $Eg_0 i$ is the optical gap at 1 min after switching off the Na lamp, and Egi is the optical gap at certain relaxation period (t_r). It is found that eqs. (6) and (7) fit the RP of Eg_1 and Eg_2, respectively, as follows:

$$Egn_1 = 0.1954 \ln t_r - 0.1791 \quad (6)$$

$$Egn_2 = 0.7082 \ln t_r - 0.9690 \quad (7)$$

For G3 samples, both the PIE on Eg and the RP of Eg, listed in Table I, can be reported as follows:

1. All of the irradiated samples exhibit a marked decrease in Eg value. This may be due to recombination of the free charge carriers (electrons and/or holes).[3]
2. The PIE on Eg value is constant for $t = 5$ to 20 min.
3. No RP have been observed for the unirradiated and the 5-min irradiated samples. This indicates that the 5-min irradiation-induced effects are persistent for 12 days at least. Thus, G3 films can be used as photorecording sensors.
4. The noticed RP, for $t \geq 10$ min, indicates that such irradiation times are not suitable for the photorecording applications.

Table I The Post-Irradiation Effect on (and the Relaxation Phenomena of) Eg (in ev) of the G3 Group

t^a	$t_r = 0^b$	$t_r = 4$	$t_r = 8$	$t_r = 12$
0	1.25	1.25	1.25	1.25
5	0.80	0.80	0.80	0.80
10	0.80	1.00	0.85	1.00
15	0.80	1.00	0.85	1.00
20	0.80	1.00	0.75	1.00

^a t is the irradiation time (in minutes).
^b t_r is the relaxation time (in days).

Our results can be discussed by the analysis of the kinetics of radiation-induced effects in the present polymer. The analysis is based on a previously suggested theoretical treatment[13] of a build-up and decay of radiation-induced conductivity (RIC) associated with the motion of free charge carriers in the presence of multiple trapping. We assume here a uniform trap distribution. In the following,[13] we review a one-dimensional model for RIC. A plane–parallel sample of polymer, of constant thickness, is exposed, beginning at time $t = 0$, to a flux of radiation producing charge carriers at a constant and uniform rate Q_0 per unit volume. Assuming a spatially homogeneous distribution of electrons and holes, the temporal evolution of charge carrier densities can be represented by the following equations.

$$\frac{dN(t)}{dt} = -k_r N_0(t)[P(t) - P_0(t)]$$

$$- \dot{k}_r P_0(t)[N(t) - N_0(t)] + Q_0 \quad (8)$$

$$\frac{\partial \rho(t, E)}{\partial t} = k_c N_0(t)[m(E) - \rho(t, E)]$$

$$- \frac{1}{\tau_r} \rho(t, E) - \dot{k}_r P_0(t) \, \rho(t, E) \quad (9)$$

$$\frac{\partial \dot{\rho}(t, E)}{\partial t} = \dot{k}_c P_0(t)[\dot{m}(E) - \dot{\rho}(t, E)]$$

$$- \frac{1}{\dot{\tau}r} \dot{\rho}(t, E) - k_r N_0(t) \, \dot{\rho}(t, E) \quad (10)$$

$$N(t) = P(t) = N_0(t) + \int_0^\infty dE \, \rho(t, E)$$

$$= P_0(t) + \int_0^\infty dE \, \dot{\rho}(t, E) \quad (11)$$

where $N(t)$ and $P(t)$ are total number densities of electrons and holes, $N_0(t)$ and $P_0(t)$ are number densities of mobile electrons with trapped holes, k_c is the rate constant for capture of mobile electrons by traps continuously distributed in energy with a density per unit energy given by $m(E)$, τ_r is the thermal release time of an electron residing on a trap with energy depth E, and

$$\tau_r = (1/v_1)\exp(E/kT) \quad (12)$$

where v_1 is the attempt-to-escape frequency (taken constant), k is the Boltzmann constant, and T is the ambient temperature. The primed quantities relate to holes.

In the post-irradiation state, assuming the absence of charge recombination,

$$t = t_p \ll 1/v_1 \exp \Psi_0$$

where t_p is the exposure time, $\Psi_0 = T_1/T$, and T_1 is the effective temperature for which kT_1 denotes the energy of the deepest traps. Then, $N_0(t)$ can be approximated by eq. (13), as follows:

$$N_0(t) \simeq C_0 t/[1 + t/t_p]$$

$$\simeq C_1 t - C_2 t \quad (13)$$

In this case, one may relate $N_0(t)$ and Eg as follows:

$$Eg \simeq C_3 + N_0(t) \quad (14)$$

where C_0, C_1, C_2, and C_3 are positive constants. Using eqs. (13) and (14), one gets

$$Eg = C_3 + C_1 t - C_2 t^2 \quad (15)$$

which agrees with the fitted values of eqs. (3) and (4) for the post-irradiation state.

In the relaxation state, solving eqs. (8)–(11), one gets at relatively long times after irradiation ($t \gg t_p$),

$$N_0(t) \propto t^{-1}$$

and

$$P_0(t) \propto t^{-1} \quad (16)$$

Using eq. (12), one can assume that N_0 (and P_0) are related to Eg by

$$N_0(t) \propto \exp(\beta Eg)$$

and

$$P_0(t) \propto \exp(\gamma Eg) \quad (17)$$

and we get

$$Eg = a - b \ln t \quad (18)$$

Figure 4 X-ray diffraction scans for films of (1) G1, (2) G1 (irradiated 5 min), (3) G2, (4) G2 (irradiated 5 min), (5) G3, (6) G3 (irradiated 5 min), and (7) G3 (irradiated 20 min).

where β, γ, a, and b are constants. Equation (18) agrees well with our fitting eqs. (6) and (7) for the relaxation states.

X-ray Diffraction

Figure 4 shows XRD scans for various PVDF films. The diffraction peaks are assigned and listed in Table II. It is noticed that all of the samples contain both of α- and β-crystalline phases of PVDF. Figure 4 implies that the 5 min of irradiation of G1 films increases the degree of crystallinity of the α-phase. This can be evidenced by the observed highest diffraction peak at $2\theta = 38.9$ degree, which was assigned to the X-ray reflections from (210) planes of α-phase.[14-16] It is noteworthy that doping PVDF with 1% $MnCl_2$ (G2 films) revealed the following double fold action: (1) the disappearance of (021) α-phase and reflections; and (2) the increase of the (210) α-phase peak, relative to that of the undoped PVDF, indicating a higher degree of α-phase crystallinity. It is remarkable that the X-ray scans of the nonirradiated G3 films exhibits a low degree of crystallinity. However, the crystallinity of G3 films increases significantly by irradiation.

Table II   Assignments[14-16] of the Peaks of X-ray Diffraction Spectra for Various PVDF Films

Sample	2θ (deg)	Assignment
G1 (nonirr)	16.8	(100) α
	18.6	(020) α
	20.5	(110), (200) β
	26.8	(021) α
	37.4	(210) α
G1 (irr 5 min)	18.4	(020) α
	20.4	(110), (200) β
	26.8	(021) α
	38.9	(002) α
G2 (nonirr)	18.8	(020) α
	20.2	(110), (200) β
	39.4	(002) α
G2 (irr 5 min)	17.7	(100) α
	20.5	(110), (200) β
	39.2	(002) α
G3 (nonirr)	20.4	(110), (200) β
	39.2	(002) α
G3 (irr 5 min)	20.4	(110), (200) β
	39.6	(002) α
G3 (irr 20 min)	20.4	(110), (200) β
	39.3	(002) α

The obtained X-ray spectra indicate that the degree of crystallinity of PVDF films is considerably influenced by the Na-irradiation, MnCl$_2$ doping, and AgNO$_3$ diffusion. These results can be explored if the modes of chelation of MnCl$_2$ and AgNO$_3$ to the PVDF chain (and their response to Na-radiation) are clarified. Liu et al.[17] reported that the phase morphology of pure PVDF basically consists of a crystalline phase, an amorphous phase, and crystal–amorphous interphase. The relative importance of these phases was found to strongly depend on annealing and addition of a diluent.

For the unirradiated PVDF (G1 films), Tawansi et al.[18,19] had observed significant roles of the free radicals on the electron spin resonance spectrum and the magnetic properties, respectively. Shapiro[20] remarked that the crystallinity of a semicrystalline polymer above the glass transition temperature is responsible for the trapping of transient species, radicals, in particular. These radicals are positively or negatively charged species. The negatively charged radicals (such as Cl$^-$, CO$^-$, CN$^-$, or F$^-$ as in the present case) are groups with significant electron affinities. The formation of radicals involves bond cleavage, such as chain scission and/or hydrogen elimination, which may lead to a decrease in polymer molecular weight, crosslinking by recombination reaction, or other side reactions, such as double bond formation.[4] In the present work, it is thought that free radicals (accumulated near the crystallite boundaries) dislocate the neighboring atoms out of their crystal sites. This builds up a shell of deformed pattern in the outermost zone of the crystallite, which reduces the effective crystalline volume. Thus, the relatively lower degree of crystallinity of G1 films is explained.

The increase of the degree of crystallinity of the irradiated G1 films appears due to the absorption of irradiation and transferring energy to the polymer, resulting in ionization, bond cleavage, and/or recombination reactions.[21] Accordingly, the previously dislocated atom, in the outer most zone of the crystallites, will return to their normal crystalline sites, increasing the degree of crystallinity. Cunha et al.[4] demonstrated that primary free radicals formed in polymers exposed to ionizing radiation can be readily oxidized by atmospheric oxygen to peroxide radicals. Maksimov et al.[22] observed that the kinetics of accumulation of peroxide radicals in the irradiated sample are determined by the rate of diffusion of oxygen and also by the rates of death of primary and formed peroxide radicals. Three types of radicals were

Figure 5 Proposed structure for PVDF–Ag$^+$ responsible for the low degree of crystallinity of G3 films.

proposed: stable nonoxidizable fluoroalkyl, stable peroxide, and unstable peroxide.

The observed increase of degree of crystallinity of G2 films, compared with G1, may be attributed to the role of MnCl$_2$ in suppressing and/or cleaning up the free radicals residing in the close vicinity of the crystallite surfaces. This suggested that the role of MnCl$_2$ can be accepted if one recalls the findings (explained in Tawansi et al.[10] and reported in the introduction of the present work) that characterize G2 films. The apparent noninfluence of irradiation on the crystallinity of G2 films may also arise from a shielding role of MnCl$_2$.[21,22]

The low degree of crystallinity of G3 films can be illustrated by assuming that the diffused AgNO$_3$ molecules may attach to PVDF chains via fluorine bridges, as shown in Figure 5.

Therefore, AgNO$_3$ is thought to play a role similar to that suggested, in the present work, for the free radicals, which dislocate the carbon atoms out of their crystalline sites and reduce the degree of crystallinity. The increased degree of crystallinity of the irradiated G3 films is attributed to fluorine bridge breaking. In this case, AgNO$_3$ may interact with oxygen and/or MnCl$_2$ to form the following structures, respectively:

$$O = Ag^+ \text{ - - - } NO_3^- \text{ - - - } [\, Ag^+ \text{ - - - } NO_3^-\,]_n \, ,$$

In these structures,[23] some of the Ag$^+$ ions were first coordinated with oxygen or chlorine, then the

Figure 6 Optical micrographs of G3 samples: (a) nonirradiated and irradiated for (b) 5 min and (c) 20 min.

of randomly oriented fibrils. These fibrils are rare in the case of nonirradiated G3 films, while irradiation increases the fibrils density. It is noteworthy that dark red-brown patches are found on the surfaces of the irradiated G3 films. The patch area increases as the irradiated time increases. These patches confirm the proposed activated complex of the diffused $AgNO_3$ in G3 films after irradiation.[24]

CONCLUSIONS

The present semicrystalline PVDF systems contain α and β phases. The degree of crystallinity is markedly affected by Na-light irradiation, $MnCl_2$ doping, and $AgNO_3$ diffusion. The post-irradiation effect and the relaxation phenomena (characterizing the optical gaps of the unfilled and 1% $MnCl_2$-filled PVDF films) were fitted numerically and agreed mathematically with a charge carrier build-up and decay model previously suggested by Tyutnev et al.[13] The $AgNO_3$ diffusion was found to stabilize the (5-min irradiation-induced) optical gap against relaxation effects. This allows one to use G3 films in photorecording applications. It was implied that $AgNO_3$ exists within the PVDF matrix in various forms, depending upon the irradiation state. For the unirradiated films, $AgNO_3$ was assumed to be connected with PVDF via the fluorine bridges. These bridges are so weak that they could be cleaved by irradiation, and activated complexes would be formed due to the attachment of $AgNO_3$ with Cl^- free radicals or oxygen (adsorbed from atmosphere).

surplus Ag^+ ions are coordinated by the NO_3^- ion. Thus, the NO_3^- ion is considered to be the bridging atom to form the activated complexes.[24]

Optical Micrography

Optical microscopy on G3 films have depicted rather interesting features, as shown in Figure 6, due to Na-light irradiation. As a common feature of the surfaces of the studied films is the presence of randomly distributed microcrystallites. It is observed that the microcrystallites can also be arranged in an ordered form, constructing a pattern

REFERENCES

1. S. Elhefnawy, Ph.D. thesis, Mansoura University, Egypt, 1995.
2. V. S. Sudarhanam and K. Srinivasan, *J. Appl. Phys.,* **68,** 1975 (1990).
3. W. Balachandran, A. Tawansi, H. Abdelkader, S. H. Elkonialy, and S. Elhefnawy, *PIE,* **2285,** 141 (1994).
4. H. N. Cunha, L. H. C. Mattoso, and R. M. Faria, *J. Polym. Sci., Part B: Polym. Phys.,* **35,** 1201 (1997).
5. H. Saito and B. Stuhn, *Polymer,* **35,** 475 (1994).
6. I. Su, Z. Y. Ma, J. I. Scheinbeim, and B. A. Newman, *J. Polym. Sci., Part B: Polym. Phys.,* **33,** 85 (1995).
7. A. Tawansi and H. M. Zidan, *J. Phys. D: Appl. Phys.,* **23,** 1320 (1990).
8. A. Tawansi and H. M. Zidan, *Int. J. Polym. Mater.,* **15,** 45 (1991).

9. E. Ahmed, A. Tawansi, and H. M. Zidan, *Physica B,* **160,** 161 (1989).

10. A. Tawansi, A. H. Oraby, E. M. Abdelrazek, M. I. Ayad, and M. Abdelaziz, *J. Appl. Polym. Sci.,* **70,** 1437–1445 (1998) .

11. G. Chiodlli and A. Magistris, *J. Solid State Ionics,* **18–19,** 356 (1986).

12. E. A. Davis and N. F. Mott, *Philos. Mag.,* **22,** 903 (1970).

13. A. P. Tyutnev, G. S. Mingaleev, A. V. Vannikov, A. F. Dunaev, V. S. Saenko, and V. S. Likhovidov, *Phys. Status Solidi A,* **75,** 385 (1983).

14. M. Ieda, T. Mizutani, and T. Naata, *1964 Annual Report of the Conference on Electrical Insulation and Dielectric Phenomena,* Claymont, DE, 1984, p. 399.

15. B. A. Newman, C. H. Yoon, K. D. Pae, and J. I. Scheinbein, *J. Appl. Phys.,* **50,** 6095 (1970).

16. S. Weinhold, M. H. Litt, and J. B. Lando, *J. Polym. Sci., Polym. Phys. Ed.,* **17,** 585 (1979).

17. Z. Liu, P. Marechal, and R. Jerome, *Polymer,* **38,** 4925 (1997).

18. A. Tawansi, M. I. Abdelkader, and E. M. Abdelrazek, *J. Mater. Sci. Technol.,* **13,** 194 (1997).

19. A. Tawansi, M. I. Abdelkader, M. Elzalabany, and E. M. Abdelrazek, *J. Mater. Sci.,* **29,** 3451 (1994).

20. A. Shapiro, *Nucl. Instrum. Methods Phys. Res.,* **B32,** 111 (1988).

21. H. J. Wintle, *IEEE Trans. Electron Insul.,* **26,** 26 (1991).

22. V. L. Maksimov, M. D. Pukshaskii, S. Y. Khaikin, and T. G. Agnivtseva, *Polym. Sci. USSR,* **27,** 518 (1985).

23. C. C. Yen, T. C. Chang, and H. Kakinoki, *J. Appl. Polym. Sci.,* **40,** 53 (1990).

24. C. J. Huang, C. C. Yen, and T. C. Chang, *J. Appl. Polym. Sci.,* **42,** 2237 (1991).