Polymer Journal, Vol. 30, No. 2, pp 149—151 (1998)

NOTES

# Excimer Fluorescence Studies on the Miscibility of Polyolefins in the Amorphous Phase

Hanying ZHAO, Zhongli LEI, and Baotong HUANG†

*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,*
*Changchun, Jilin, 130022, People's Republic of China*

(Received May 24, 1997)

KEY WORDS Linear Low-Density Polyethylene / High-Density Polyethylene / Ethylene and Methacrylic Acid / Blends / Excimer Fluorescence /

Polymer miscibility is generally related to its amorphous.[1] Miscibility studies of partially crystalline polymer blends are complex due to the presence of amorphous and crystalline regions. The blending of different polyolefins has aroused much interest and academic articles and patents on polyolefin blends are numerous.[2-4] Much attention has been focused on the crystallization behavior of polyolefin blends.[5] However, study of miscibility of polyolefins in the amorphous phase is much neglected. Melt viscosity and mechanical properties have frequently been used to predict the miscibility of polymer blends.[3] Higgins *et al.*,[6] used neutron scattering to study the miscibility of various polyethylene blends. In this paper (1) blends of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), and (2) blends of LLDPE and random copolymer of ethylene and methacrylic acid (EMA) were studied by excimer fluorescence. To our knowledge this is the first study on the miscibility of the amorphous phase in polyolefin blends by excimer fluorescence.

## EXPERIMENTAL

### *Materials*

LLDPE was purchased from Daqing Petrochem. Co., with a molecular weight of $1.67 \times 10^5$ ($M_w$, measured by GPC on PS standards).

HDPE in this study was kindly supplied by DSM Co. in Holland. The molecular weight of HDPE is approximately $8 \times 10^4$ as determined by GPC.

The ethylene–methacrylic acid copolymer was originally an ionic salt of a copolymer of ethylene and methacrylic acid under the trade name Surlyn. The content of methacrylic acid (MAA) was 15.2 wt%, 18.04% of which was in the form of zinc salt, as determined by elementary analysis and atomic spectroscopy. Its molecular weight was $2.52 \times 10^4$ ($M_w$, measured by GPC on PS standards). The completely nonionized copolymer (EMA) was obtained by adding sulfuric acid in THF to Surlyn in xylene solution at 55°C.

Aminonaphthalene was purchased from Xing-zhong Chemical Factory in Shanghai, China. Maleic anhydride was purchased from Chemical Reagents Factory in Shenyang, China. Fluorescence emission spectra of aminonaphthalene and reaction product of aminonaphthalene with maleic anhydride in tetrahydrofuran (THF) are shown in Figure 1. At high concentration, only broad excimer fluorescence at about 400 nm was observed. However, at low chromophore concentration excimer and monomer fluorescence at 340 nm were both observed.

Naphthalene-labeled LLDPE: LLDPE was first grafted with maleic anhydride (MA) in the presence of benzoyl peroxide in xylene at 120°C to 2 wt%. LLDPE-*g*-MA was reacted with aminonaphthalene in toluene at 110°C under argon atmosphere for 2 h. The content of aromatic rings on the LLDPE chains was about 1 mol% (measured by $^1$H NMR).

Labeled polymer was purified by repeated dissolving and precipitation cycles (5 times) using a system of xylene/alcohol (solvent and precipitating agent, respectively).

### *Blending*

LLDPE/HDPE and LLDPE/EMA blends were prepared by dissolving the components in xylene at 120°C under argon atmosphere to yield dilute solutions, precipitated by pouring the solution into alcohol, filtered, and dried under vacuum for a week at 70°C.

### *Measurements*

The blends in the fluorescence study were compression molded at 140°C for 5 min and cooled slowly to room

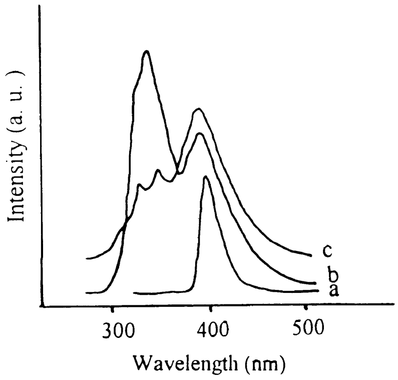

**Figure 1.** Emission spectra of aminonaphthalene and reaction product of aminonaphthalene with maleic anhydride in THF solutions on excitation at 295 nm. Curve a for aminonaphthalene at $1 \times 10^{-4}$ g ml$^{-1}$; curve b for aminonaphthalene at $2.28 \times 10^{-6}$ g ml$^{-1}$; curve c for reaction product of aminonaphthalene with maleic anhydride at $4 \times 10^{-7}$ g ml$^{-1}$.

---

† To whom all correspondence should be addressed.

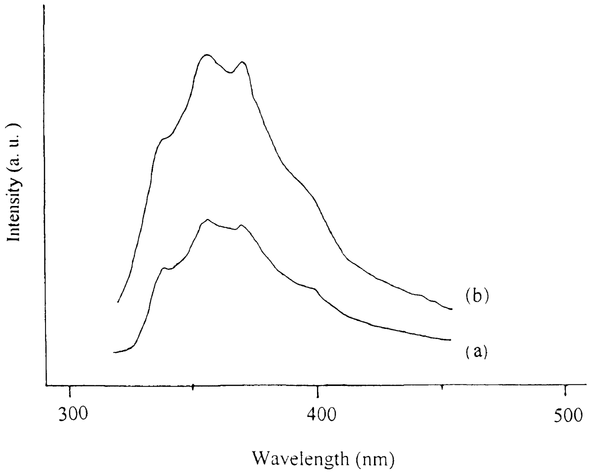

**Figure 2.** Uncorrected emission spectra of chromophore-labeled LLDPE/EMA blends upon excitation at 295 nm. Curve a for 90/10 LLDPE/EMA blends and curve b for 50/50 blends.

temperature. Quenching tests were carried out by dipping the samples at high temperatures into liquid nitrogen. Emission spectra were measured at room temperature on a Shimadzu RF-5000 fluorescence spectrometer.

## RESULTS AND DISCUSSION

Excimer fluorescence is a powerful tool for investigating polymer blend compatibility.[7-10] An excimer is an excited molecular complex formed between two identical aromatic rings, one of which is in a singlet excited state.[11] In polymer blends containing chromophore-labeled polymers, excimer sites may form: (1) through intermolecular interactions between aromatic rings on different chains, (2) from intramolecular interactions between rings on nonadjacent chain segments, or (3) between aromatic rings on adjacent segments. The number of excimer sites is proportional to the ratio of excimer emission intensity ($I_D$) to emission intensity of the isolated "monomer" ($I_M$). In naphthalene-labeled polymers, these values were 400 and 340 nm, respectively.

Intramolecular interactions between aromatic rings depend upon conformations of polymer chains, so the intramolecular excimer plays an important role in expansion of polymer chains in dilute solution.[12,13] The intermolecular excimer sites arising from clustering of polymer chains are sensitive to aggregation of aromatic rings. In miscible polymer blends, interpenetration of different chains causes local concentration of aromatic rings to drop.

In chromophore-labeled LLDPE/HDPE and chromophore-labeled LLDPE/EMA blends, the aromatic rings labeled on LLDPE chains cannot enter crystalline regions and they only exist in amorphous regions. So change in excimer to monomer ratio ($I_D/I_M$) indicates the interpenetration of chromophore-labeled LLDPE chains with HDPE chains and that with polyethylene (PE) segments of EMA in amorphous phase. Thus, miscibility of LLDPE/HDPE and LLDPE/EMA blends in the amorphous phase can be probed.

Figure 2 shows typical uncorrected emission spectra of chromophore-labeled LLDPE/EMA blends. The peak at 340 nm corresponds to the isolated naphthalene "monomer" and the broad band at 400 nm corresponds to the excimer complex. The peaks of excimer and monomer fluorescence lie on the slope of fluorescence peaks at 372 nm and 355 nm. Assuming all peaks to be Gaussian in shape, corrected monomer and excimer blends can be obtained by fitting a spectrum to the separated functional forms,[14] and $I_D/I_M$ can be compared.

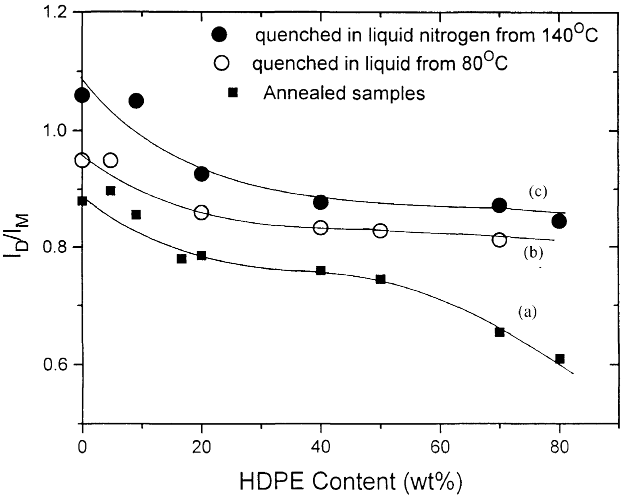

**Figure 3.** Excimer to monomer intensity ratio *vs.* weight percent HDPE. Curve a, samples annealed from 140°C to room temperature; curve b, samples quenched in liquid nitrogen from 80°C; curve c, samples quenched in liquid nitrogen from 140°C.

Hu *et al.*[5] studied binary blends of LLDPE and HDPE blends. They proved cocrystallization between LLDPE and HDPE components. The mechanical $\alpha$, $\beta$, and $\gamma$ relaxation of the blends shows that the 50/50 blend displays intermediate relaxation behavior between those of the components in all $\alpha$, $\beta$, and $\gamma$ regions. This shows the characteristic of a typical miscible blend.

For blends annealed from 140°C to room temperature, our experiments showed a $I_D/I_M$ decrease with increasing HDPE in blends of chromophore-labeled LLDPE and HDPE (Figure 3), suggesting a decrease in the number of excimer sites upon adding HDPE. LLDPE chains in the amorphous region are diluted by HDPE chains added.

For samples quenched in liquid nitrogen from 80°C or 140°C, $I_D/I_M$ decreases with the addition of HDPE. For quenched samples, the states of molecular chains at a high temperature are frozen when the samples are quenched in liquid nitrogen. Decrease in $I_D/I_M$ means HDPE chains can still penetrate LLDPE domains even at high temperatures.

A few papers have appeared on blends of EMA and polyethylene. Fairley *et al.*[15] studied binary LDPE/EMA blends. Their results show that no interactions between the crystalline components of the mixtures exist, and only weak interactions exist in the amorphous region.

Figure 4 shows the average value of the excimer to monomer ratio ($I_D/I_M$) plotted against EMA content (by wt%) in LLDPE/EMA blends. For blends annealed very slowly from 140°C to room temperature, $I_D/I_M$ decreases with the addition of EMA, indicating drop in local concentrations of naphthalene rings in the amor-

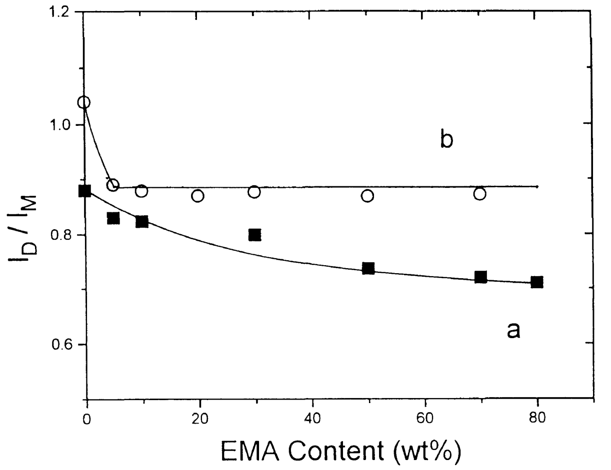

**Figure 4.** Excimer to monomer intensity ratio *vs.* weight percent EMA. Curve a, samples annealed from 140°C to room temperature; curve b, samples quenched in liquid nitrogen from 140°C.

phous phase (curve a in Figure 4) and EMA/LLDPE blends are miscible in the amorphous phase at room temperature. For blends quenched in liquid nitrogen from 140°C, $I_D/I_M$ almost keeps constant when EMA is in the range of 5—70% (curve b in Figure 4). The constant $I_D/I_M$ means PE chains in EMA do not penetrate LLDPE domains in the amorphous phase at high temperature, and EMA and LLDPE are immiscible at high temperature.

*Acknowledgment.* This study was supported by National Sciences Foundation of China by Grant No. 59503002 and Polymer Physics Laboratory of Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. We express our thanks to Dr. Weidong Liu for his help and comments.

## REFERENCES

1. O. Olabisi, L. M. Robeson, and M. T. Shaw, "Polymer–Polymer Miscibility," Academic, New York, N.Y., 1979.
2. A. Plochocki, in "Polymer Blends," D. R. Paul and S. Newman, Ed., Academic, New York, N.Y., 1978, p 319.
3. T. Kyu and P. Vadhar, *J. Appl. Polym. Sci.*, **32**, 5575 (1986).
4. M. Ree, T. Kyu, and R. S. Stein, *J. Polym. Sci., Polym. Phy. Ed.*, **25**, 105 (1987).
5. S.-R. Hu, T. Kyu, and R. S. Stein, *J. Polym. Sci., Polym. Phy. Ed.*, **25**, 71 (1987).
6. J. S. Higgins and R. S. Stein, *J. Appl. Crystallogr*, **11**, 346 (1978).
7. S. N. Semerak and C. W. Frank, *Macromolecules*, **14**, 443 (1981).
8. M. A. Gashgari and C. W. Frank, *Macromolecules*, **14**, 1558 (1981).
9. P. D. Fitzgibbon and C. W. Frank, *Macromolecules*, **15**, 733 (1982).
10. R. Gelles and C. W. Frank, *Macromolecules*, **15**, 1486 (1982).
11. C. W. Frank and M. A. Gashgari, *Macromolecules*, **12**, 163 (1979).
12. R. Qian and X. Gu, *Angew. Makromol. Chem.*, **141**, 1 (1986).
13. H. Y. Zhao, Z. L. Lei, F. J. Song, and B. T. Huang, *Chinese J. Appl. Chem.*, **4**, 29 (1997).
14. R. Gelles and C. W. Frank, *Macromolecules*, **16**, 1448 (1983).
15. G. Fairley and R. E. Prud'homme, *Polym. Eng. Sci.*, **27**, 1495 (1987).