

# Macromolecular Research

Volume 11, Number 5    October 31, 2003

© Copyright 2003 by The Polymer Society of Korea

---

## Effect of Thermal Imidization and Curing on Fluorescence Behavior of a Phenylethynyl-Terminated Poly(amic acid)

Donghwan Cho\* and Gyeongmo Yang

*Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Kumi, Kyungbuk 730-701, Korea*

Lawrence T. Drzal

*Composite Materials and Structures Center, Michigan State University, E. Lansing, MI 48824-1226, U.S.A.*

*Received Nov. 18, 2002; Revised July 25, 2003*

**Abstract:** The imidization and cure reaction of a thermosetting phenylethynyl-terminated amic acid (LaRC PETI-5) in film form have been monitored as a function of temperature by means of a steady-state fluorescence technique using a front-face illumination method. The variation of the fluorescence emission spectra of LaRC PETI-5 can be divided into four temperature regions; Region I: below 150 °C, Region II: 150-250 °C, Region III: 250-350 °C, and Region IV: above 350 °C. The fluorescence spectra in Region I are largely influenced by residual *N*-methyl-2-pyrrolidinone in the polymer and also slightly by partial imidization of the polymer. There is a combined effect of imidization and solvent removal on the fluorescence behavior in Region II. The spectra in Regions III and IV are due significantly to the cure reaction of LaRC PETI-5 and to a post-cure effect of the polyimide, respectively. This spectroscopic evidence indicating the transformation of the amic acid imide oligomer into the corresponding polyimide via imidization and cure, agrees well with thermal analysis results obtained previously. The intermediate stage of cure in the range of 250-300 °C predominantly influences the change of the fluorescence intensity. The later stage above 300 °C significantly influences the position of the spectrum. This fluorescence study also supports the mechanism proposed in earlier work that the crosslinking reaction takes place at the reaction sites in the conjugated polyene and the phenylethynyl end group in the polyimide chain.

*Keywords:* fluorescence, imidization, cure, phenylethynyl-terminated imide oligomer.

### Introduction

Phenylethynyl-terminated polyimides, which have been developed at the National Aeronautics and Space Adminis-

tration (NASA) Langley Research Center several years ago and increasingly considered as a new generation of acetylene terminated thermosetting polyimides, have potential use not only in aerospace and aircraft industries but also as advanced composite matrix resins, adhesives and sizings because of their high temperature and processing performance.<sup>1-4</sup> A number of research publications have been made with the

---

\*e-mail : dcho@knut.kumoh.ac.kr

1598-5032/10/297-06©2003 Polymer Society of Korea

objective of understanding the reactions and properties of uncured and cured resins of phenylethynyl-terminated polyimides.<sup>5-9</sup> These studies include cure, end group reaction behavior, thermal properties, mechanical properties, interfacial characteristics, etc.

Fluorescence techniques have been frequently used as convenient and reliable tools for investigating the cure reaction or crosslinking behavior of thermosetting polymers. This is due to the fact that the fluorescence behavior sensitively depends on the change of the microenvironment of the intrinsic or extrinsic fluorophores associated with the extent of cure or aggregation.<sup>10</sup> There have been many reports on characterizing cure behavior of thermosetting polymers such as epoxy,<sup>11,12</sup> polyimide,<sup>13,14</sup> vinyl ester,<sup>15</sup> polyurethane,<sup>16</sup> etc. by means of fluorescence techniques. The materials with a fluorescing moiety in the molecule undergo chemical reactions with the subsequent changes in their substitution groups attached to the aromatic ring, resulting in the change of fluorescence spectrum with the extent of cure. One approach relies on the enhancement of fluorescence intensity with increasing matrix viscosity or molecular interaction due to a decrease in radiationless deactivation of the excited state.<sup>17</sup> Such a fluorescence enhancement often allows one to monitor the reaction behavior during imidization and cure, specifically in thermally curable polyimides.

In this paper, we characterize the steady-state fluorescence behavior of a phenylethynyl-terminated amic acid (LaRC PETI-5) on thermal curing. In a previous study, Cho and Drzal have found that fiber-matrix interfacial properties in carbon fiber/BMI composites can be significantly improved by incorporating LaRC PETI-5 as a high temperature sizing material for better processing and interfacial properties.<sup>18</sup> It has been expected that the improvement of the interfacial properties may be explained by interdiffusion at the interface between the BMI matrix resin and the LaRC PETI-5 sizing interphase. This interdiffusion has been demonstrated by using this fluorescence technique in an earlier report.<sup>19</sup> In conjunction with the result, the objective of this study is to provide a better understanding of the relationship of fluorescence behavior to the molecular behavior during imidization and cure reaction of LaRC PETI-5 and also to support the proposed mechanism for crosslinking reaction of a thermosetting LaRC PETI-5 resin, based upon the photophysical result from the intrinsic fluorescence of the material.

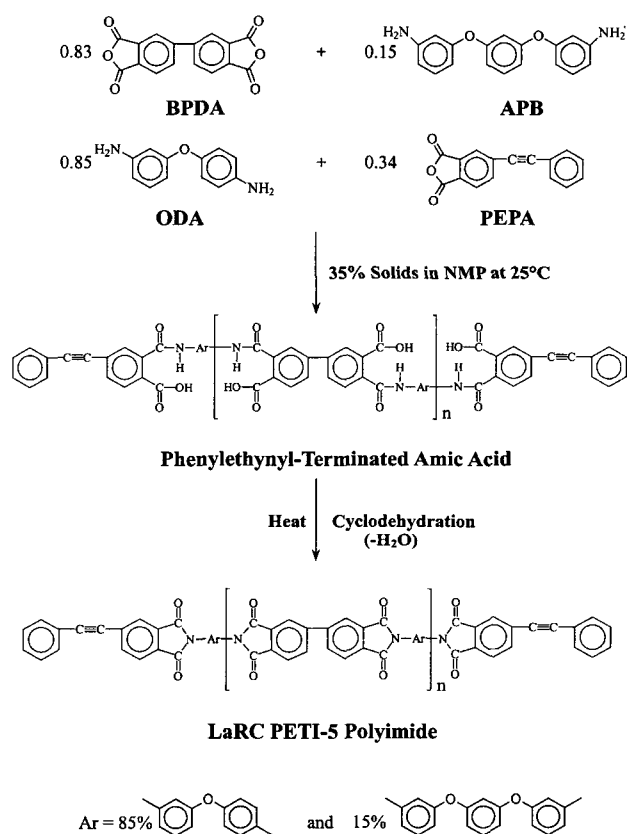
## Experimental

**Materials.** The phenylethynyl-terminated imide oligomer used in this work was synthesized and supplied in the liquid form of an amic acid from Imitec, Inc. (Schenectady, NY). The as-received LaRC PETI-5 is a random copolymer with a number-average molecular weight of 2500 g/mol, which is prepared from 3,4-oxydianiline (ODA), 1,3-bis(3-aminophenoxy)benzene (APB), and 3,3',4,4'-biphenyltetracarboxylic

dianhydride (BPDA), endcapped with 4-phenylethynylphthalic anhydride (PEPA). The synthesis and chemistry of LaRC PETI-5 have been described in detail elsewhere.<sup>4</sup> The solids content in *N*-methyl-2-pyrrolidinone (NMP) as solvent is about 35% by weight. Figure 1 represents the chemical structures of the components, amic acid and polyimide of LaRC PETI-5.

**Sample Preparation.** The as-received amic acid oligomer was kept in a freezer and warmed to ambient temperature immediately prior to use. A thin, uniform film of the as-received LaRC PETI-5 resin was formed on a glass plate using a doctor blade. The glass plates with the thin film samples were subsequently heated up to 400°C in steps of 50°C in air. The cure time at each temperature was 1 hr. This procedure resulted in a sample that was exposed to cumulatively greater degree of polymerization at each given cure temperature prior to each fluorescence measurement.

**Steady-State Fluorescence Measurement.** Steady-state fluorescence spectra of each film were observed at ambient temperature in air using an Aminco-Bowman Series 2 Luminescence Spectrometer equipped with a pulsed xenon lamp as light source. A front-face illumination method with an incident angle of 24° was utilized. The slit widths were 4 nm for excitation and 8 nm for emission, respectively. The



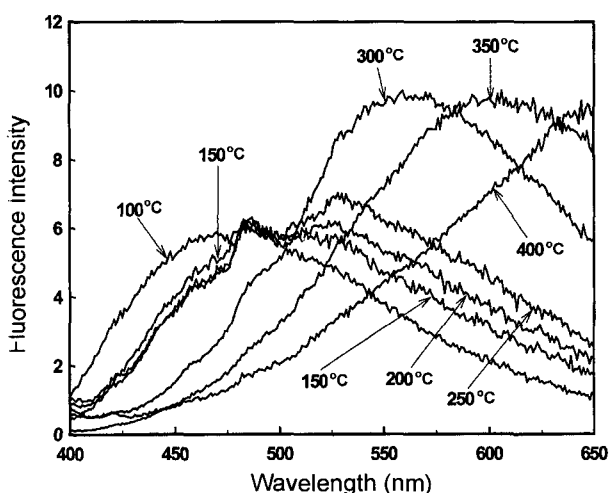
**Figure 1.** Chemical structures of the components, amic acid oligomer, and polyimide of LaRC PETI-5.

excitation wavelength was 368 nm. The emission spectrum for each sample was scanned from 400 to 650 nm. The fluorescence spectra were corrected for the wavelength-dependent instrumental response and for the wavelength distribution of xenon lamp intensity. No extrinsic cure monitorable fluorescence probe and polarizer were applied in this system. All the samples for fluorescence measurements were prepared with the same methodology and observed using identical instrumental parameters so that meaningful comparisons could be made. The only variation given to each sample was a different cure history.

**Results**

Figure 2 shows the variations of fluorescence emission spectra as a function of wavelength measured for LaRC PETI-5 at different cure temperatures. The LaRC PETI-5 amic acid oligomer heated at 100°C exhibits more or less a structureless broad emission band with a maximum near 480 nm. The size and shape of the spectrum for the as-received oligomer were observed to be almost similar to this band without significant change. It is noted that there are two distinguishable changes in the spectral shape and size and the maximum wavelength with varying cure temperature from 100 to 400°C. One is a prominent reduction of the fluorescence intensity below 500 nm and the other is a strong enhancement of the intensity near 527 nm and a large red-shift of the peak to longer wavelength.

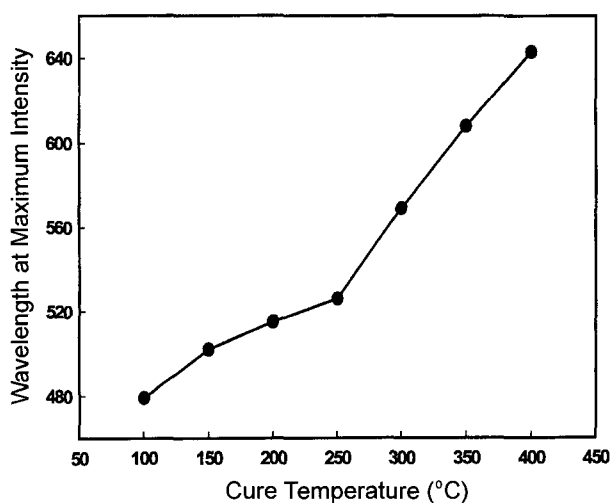
Figure 3 plots the change of wavelength at the maximum fluorescence intensity as a function of cure temperature. As can be seen, there is a large red-shift of about 165 nm in the maximum wavelength from 480 nm at 100°C to 645 nm at 400°C, showing a notable break at 250°C. This result indicates that curing LaRC PETI-5 imide oligomer leads to a significant shift of fluorescence spectra to longer wavelength



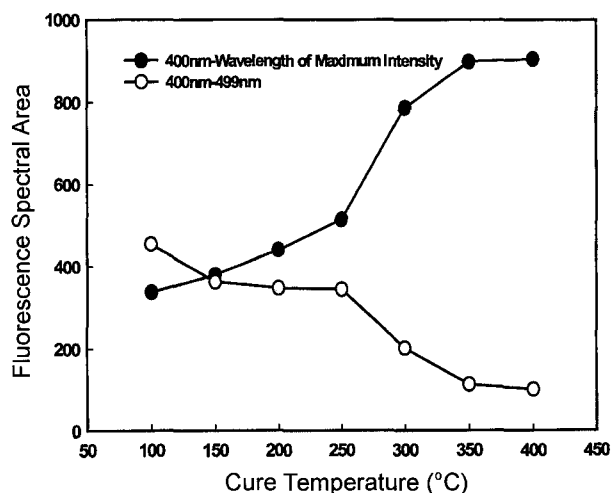
**Figure 2.** Steady-state fluorescence spectra observed for LaRC PETI-5 films thermally cured at different temperatures.

with increasing temperature.

Figure 4 represents the variations of the spectral area of fluorescence of LaRC PETI-5 with increasing cure temperature. The spectral areas were calculated in two different regions from each spectrum of Figure 2. One is from 400 nm to the wavelength at the maximum intensity of each fluorescence band. Such a region was selected to minimize possible uncertainty in calculating the spectral area, which can be resulted from the tails of the spectra (100 to 250°C) and also from the large portion of spectral bands (300 to 400°C) beyond their maximum. There was no difficulty in analyzing each spectrum in the regions because it is likely to be quite symmetrical with tails in the longer wavelength portion. The other region was selected to be from 400 to 499 nm to emphasize the change of the fluorescence emission located in



**Figure 3.** Effect of cure temperature on the red-shift of the fluorescence spectrum of LaRC PETI-5 films.



**Figure 4.** Variations of the fluorescence spectral area as a function of cure temperature for LaRC PETI-5.

the shorter wavelength region. Understanding the change of the spectral area in this region will provide useful information on the imidization of LaRC PETI-5 resin as well as the removal of NMP solvent. As can be seen, the spectral area of fluorescence emission from 400 nm to the wavelength at the maximum intensity slightly increases to 150 °C and then continuously increases to 250 °C. It is also found that there is an obvious break at 250 °C. Above 250 °C, the spectral area increases abruptly to 300 °C, increases at a slower rate up to 350 °C, and then levels off with a largest spectral area. The spectral area obtained from 400 to 499 nm varies in a similar manner.

## Discussion

Combining all the results shown in Figures 2-4, the variations of the fluorescence emission spectra of LaRC PETI-5 can be described into four different temperature regions as follows, reflecting transformation of the amic acid oligomer into the corresponding polyimide via imidization and cure: Region I: below 150 °C, Region II: 150-250 °C, Region III: 250-350 °C, and Region IV: above 350 °C.

It is generally known that the imidization reaction of poly(amic acid) in solid state is very slow around 100 °C and largely increases above 150 °C.<sup>20</sup> At this stage, the molecular state of imide chains alters significantly. It may play an important role in the fluorescence behavior of interest because fluorescence depends on the changes of molecular environments by physical causes as well as by chemical causes. The fluorescence spectra in the Region I are largely influenced by NMP solvent contained in the LaRC PETI-5 amic acid oligomer, and also to some extent by partial imidization of the oligomer. NMP is not completely removed below 200 °C because the boiling point of NMP is 202 °C. However, a large portion of NMP can be evaporated between 100 and 150 °C, and additionally between 150 and 200 °C as demonstrated using differential scanning calorimetry (DSC)<sup>21</sup> and Fourier Transform infra-red (FT-IR)<sup>22</sup> earlier. Such a decrease of the solvent involved in the system can be deduced from the spectral change in Figure 2, and also from the curve (open circles) in Figure 4. It is unlikely that partial imidization significantly influences the fluorescence emission in the spectral range below 500 nm. It influences the emission band above 500 nm, as discussed later.

The combined effects of imidization and solvent removal influence the fluorescence spectra in Region II. The extent of imidization gradually increases with temperature to 250 °C. It indicates that the amic acid oligomer begins to imidize below 200 °C and completes its imidization reaction at 250 °C. Therefore, the major contribution in this region may be by imidization, which can be significant above 200 °C and the minor contribution may be by solvent, which can be significant far below 200 °C. This fluorescence result also confirms that the LaRC PETI-5 amic acid oligomer is imi-

dized to form the corresponding LaRC PETI-5 polyimide on heating, as observed from thermal analysis studies earlier.<sup>6,21</sup>

With the development of the imidized structure in the resin, the fluorescence emission band at wavelengths above 500 nm is enhanced with a long wavelength tail, as seen in Figure 2. The maximum of the fluorescence intensity is shifted to the longer wavelength about 30 nm due to the imidization reaction, as shown in Figure 3. The spectral area of the fluorescence from 400 nm to the peak maximum is increased (closed circles) but that from 400 to 499 nm (open circles) is slightly decreased showing a plateau, as shown in Figure 4. The fluorescence behavior in Region II indicates that the presence of a very small amount of the NMP solvent does not significantly influence the shorter wavelength band of the fluorescence spectrum but the imidization plays an important role in the longer wavelength band of the fluorescence. This result illustrates that the fluorescence technique can provide a useful method to determine the complete imidization temperature for transformation of an amic acid into a corresponding polyimide, as demonstrated by the breaks at 250 °C in Figures 3 and 4. The enhancement of fluorescence intensity becomes pronounced with increasing imidization temperature or heat-treatment temperature. Such an enhancement in the fluorescence of LaRC PETI-5 can be explained by the formation of charge transfer complexes occurring during the imidization process, as studied with different aromatic polyimide systems by others.<sup>10,20,23-25</sup> In the LaRC PETI-5 chain, the anhydride moieties in the BPDA and PEPA molecules play a role as electron acceptor and the diamine moieties in the APB and ODA molecules as electron donor.

The fluorescence spectrum in Region III is primarily attributed to cure reaction of LaRC PETI-5 oligomer, which is activated around 300 °C. It may lead to further enhancement of the fluorescence intensity due to the higher concentration of the charge transfer complexes. There are three factors supporting this interpretation. First, the significant enhancement of the fluorescence emission band is observed for the samples cured above 300 °C, as seen in Figure 2. Second, there is a large red-shift of the wavelength at the maximum intensity of fluorescence, as shown by a higher slope beyond the break point at 250 °C in Figure 3. Third, the spectral area of the fluorescence abruptly changes after 250 °C, as seen by the closed circles in Figure 4. A decrease of the spectral area is due to the red-shift of the fluorescence emission band.

As the cure temperature exceeds the imidization temperature, the formation of a crosslinked structure between C≡C bonds in the reactive phenylethynyl group located at the imide polymer chain ends proceeds causing a large restriction of chain flexibility until the cure reaction is complete. Such the fact has been experimentally demonstrated from earlier reports<sup>6,21,22</sup> independently studied using FT-IR, DSC and dynamic mechanical analysis (DMA) technique. The results showed that the cure reaction involving crosslinking and chain extension by a reaction of C≡C bonds in the phe-

nylethynyl end groups is completed as LaRC PETI-5 resin is heated at 350 °C for 1 hr. Consequently, the reduction of the flexibility of the polymer chain at the intermediate stages of cure may cause further rigidization of the fluorescing imide chains and intermolecular interaction between polyimide chains, resulting in the enhanced fluorescence intensity.

Combining the present fluorescence results seen in Figures 2-4 and the previous results obtained from thermal analysis studies, it can be concluded that the range of 250-300 °C, which is the intermediate stage of cure, is most responsible for the enhancement of the fluorescence intensity of LaRC PETI-5. It has been found that the glass transition temperature ( $T_g$ ) of LaRC PETI-5 polyimide is 280 °C by DSC<sup>21</sup> and 287 °C by DMA,<sup>6</sup> respectively. Therefore, it may be deduced that the fluorescence intensity increases with decreasing chain flexibility prior to the glass transition. Above the  $T_g$ , the fluorescence intensity is not significantly affected but the spectrum is significantly shifted to higher wavelength. The red-shift of the fluorescence emission peaks in the range of 250-300 °C is probably explained by a decrease of intermolecular distance in the charge transfer complex formed with increasing cure temperature.

This result, showing a large enhancement of the fluorescence intensity in Region III, agrees well with the previous results. DSC<sup>21</sup> and DMA<sup>6</sup> studies showed that the extent of cure largely increases in the range of 250-300 °C and increases the greatest in the range of 300-350 °C, where the reaction of the phenylethynyl end groups predominates. FTIR spectroscopy studies<sup>22</sup> revealed that C≡C bonds in the phenylethynyl end groups in the LaRC PETI-5 polymer chain are responsible for the cure reaction involving crosslinking and chain extension. Also, the C≡C bonds located in the phenylethynyl group are converted into C=C bonds with increasing cure temperature around 300 °C, and then finally disappear at 350 °C.

It has been proposed that the network structure can be formed by the crosslinking reaction among the reactive sites in the conjugated polyene and phenylethynyl end group.<sup>1,22</sup> However, the proposed structure and mechanism have not been clarified. The fluorescence result in the present work demonstrates that such a crosslinking scheme proposed earlier may be reasonable from a photophysical viewpoint. With increasing cure temperature above 300 °C, the intermolecular distance in the intermolecular charge transfer complex decreases. In addition to this, it may be considered that the conjugation length owing to the converted C=C bonds and the aromatic imide polymer chains increases. An increase of the conjugation length is energetically favorable due to the extended delocalization of electrons. This will make the structure of LaRC PETI-5 more stable with a lower energy state, resulting in an additional red-shift of the fluorescence emission spectrum.

In Region IV, the fluorescence emission band is further red-shifted at 400 °C without a significant change of the

intensity. This can be explained in a similar manner with the fluorescence behavior seen between 300 and 350 °C in Region III. This is likely ascribed to an additional red-shift due to a post-curing effect of LaRC PETI-5 polyimide. Subsequent heating to a higher temperature prior to decomposition will result in the additional formation of crosslinked structure between very small, uncured polyimide chains. The cure behavior depicted by closed circles in Figure 4 shows a similar shape with the degree of cure behavior studied using DSC<sup>21</sup> earlier. However, the shapes are not overlapped exactly due to different mechanism between the two analytical methodologies.

## Conclusions

The variations of the fluorescence emission spectra of the phenylethynyl-terminated polyimide prepared with different cure history can be divided into four temperature regions; Region I: below 150 °C, Region II: 150-250 °C, Region III: 250-350 °C, and Region IV: above 350 °C.

The fluorescence spectra in Region I are influenced predominantly by NMP solvent contained in the LaRC PETI-5 amic acid oligomer, and also to some extent by partial imidization of the oligomer. On the other hand, the imidization is a main contributing factor on the fluorescence spectra observed in Region II, and the presence of a small amount of the solvent is a minor factor. The increase in fluorescence intensity at the longer wavelength above 500 nm along with a red-shifted maximum is resulted from the development of the imidized structure in the LaRC PETI-5 material.

The fluorescence spectra in Region III are due primarily to the cure reaction of the LaRC PETI-5 polyimide. An increase of cure temperature up to near 300 °C, beyond the  $T_g$  of the polymer, leads not only to further enhancement of the fluorescence intensity but also to a significant red-shift of the spectrum. The former may be explained by a higher concentration of the intermolecular charge transfer complexes formed between the electron-accepting anhydride moiety and the electron-donating diamine moiety with cure. The latter may be explained by a decrease of intermolecular distance in the charge transfer complex. It is concluded that the intermediate stage of cure in the range of 250-300 °C influences the fluorescence intensity and the later stage above 300 °C influences the position of the spectrum. The present fluorescence results provide qualitative information on the degree of imidization and the degree of cure.

It is also worth noting that a proposed crosslinking reaction between the reactive sites in the conjugated polyene and the phenylethynyl end groups in the LaRC PETI-5 polyimide chain is supported by the fluorescence method in the present work.

**Acknowledgements.** This research was sponsored by the Air Force Office of Scientific Research, Air Force Material

Command, USAF, under grant number F49620-98-1-0377.

## References

- (1) P. M. Hergenrother and J. G. Smith, Jr., *Polymer*, **35**, 4857 (1994).
- (2) B. J. Jensen, R. G. Bryant, J. G. Smith, Jr., and P. M. Hergenrother, *J. Adhesion*, **54**, 57 (1995).
- (3) P. M. Hergenrother, *SAMPE J.*, **35**(1), 30 (1999).
- (4) J. W. Connell, J. G. Smith, Jr., and P. M. Hergenrother, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, **C40**, 207 (2000).
- (5) M. L. Rommel, L. Konopka, and P. M. Hergenrother, *28<sup>th</sup> Intl SAMPE Technical Conference*, Nov. 4-7, 1 (1996).
- (6) D. Cho, Y. Choi, and L. T. Drzal, *Polymer*, **42**, 4611 (2001).
- (7) X. Fang, D. F. Rogers, D. A. Scola, and M. P. Stevens, *J. Polym. Sci.: Part A: Polym. Chem.*, **86**, 461 (1998).
- (8) A. C. Chang and B. J. Jensen, *J. Adhesion*, **72**, 209 (2000).
- (9) J. A. Hinkley and D. A. Proctor, *J. Adv. Mater.*, **32**(4), 35 (2000).
- (10) E. D. Wachsman and C. W. Frank, *Polymer*, **29**, 1191 (1998).
- (11) K.-F. Lin and F. W. Wang, *Polymer*, **35**, 687 (1994).
- (12) D. Cho, D. S. Kim, and J. K. Lee, *Polymer(Korea)*, **25**(2), 199 (2001).
- (13) R. J. Mathisen, J. K. Yoo, and C. S. P. Sung, *Macromolecules*, **20**, 1414 (1997).
- (14) S. M. Pyo, T. J. Shin, S. I. Kim, and M. Ree, *Mol. Cryst. Liq. Cryst.*, **316**, 353 (1998).
- (15) J. L. Jessop, A. B. Scranton, and G. J. Blanchard, *Polym. Mater. Sci. Eng.*, **72**, 58 (1995).
- (16) R. Vatanparast, S. Li, K. Hakala, and H. Lemmetyinen, *Macromolecules*, **33**, 438 (2000).
- (17) A. Stroeks, M. Shmorhun, A. M. Jamieson, and R. Simha, *Polymer*, **29**, 467 (1988).
- (18) D. Cho, Y. Choi, and L. T. Drzal, *J. Adhesion*, **79**, 1 (2003).
- (19) D. Cho, G. Yang, and L. T. Drzal, *Polym. Mater. Sci. Eng.*, **87**, 283 (2002).
- (20) T. J. Shin, B. Lee, H. S. Youn, K.-B. Lee, and M. Ree, *Langmuir*, **17**, 7842 (2001).
- (21) D. Cho and L. T. Drzal, *J. Appl. Polym. Sci.*, **75**, 1278 (2000).
- (22) D. Cho and L. T. Drzal, *J. Appl. Polym. Sci.*, **76**, 190 (2000).
- (23) M. Hasegawa, H. Arai, I. Mita, and R. Yokota, *Polym. J.*, **22**, 875 (1990).
- (24) M. Hasegawa and K. Horie, *Prog. Polym. Sci.*, **26**, 259 (2001).
- (25) M. Hasegawa, M. Kochi, I. Mita, and R. Yokota, *Eur. Polym. J.*, **25**, 349 (1989).