*Korean J. Chem. Eng.*, **22**(5), 750-754 (2005)

# Photopolymerization of Thermoplastic Polyurethane/Acrylate Blends

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(*Received 6 January 2005 • accepted 7 June 2005*)

**Abstract**−The kinetics of photopolymerization of thermoplastic polyurethane/acrylate blends have been studied using Real Time - Fourier Transform Infrared Spectroscopy (RT-FTIR). The polymerization rate curves were autocatalytic in nature at the initial stage of reaction; then a retardation of the reaction conversion occurred gradually as the polymer matrix became vitrified and the reaction became diffusion controlled. A kinetic rate equation with a diffusion control factor term has been employed to characterize the diffusion-controlled reaction behavior. As the reaction conversion reaches the transition point, at which the maximum value of $k_p/k_t^{0.5}$ in the rate expression is obtained, the reaction becomes to be controlled by diffusion due to the restricted mobility of acrylate macromonomers, resulting in the rapid drop of the polymerization rate even keeping the same reactivity of all the double bonds of acrylate macromonomers. Interpenetrating polymer networks (IPNs) of thermoplastic polyurethane/acrylate systems were formed in the limit of TPU content in the formulations. As the content of thermoplastic polyurethane increased, the polymerization rate increased in the early stage of cure reaction. Blends containing polyurethane up to 30 phr have single glass transition temperature, which indicates that they are miscible in blends and no phase separation has been observed.

Key words: Photopolymerization, Thermoplastic Polyurethane, Diffusion Control Reaction, IPNs, Phase Separation

## INTRODUCTION

The photopolymerization of acrylate macromonomers leads to highly crosslinked networks, and radiation cured systems are currently used on plastics for vinyl floor tile, credit cards, compact discs, release film, and plastic labels. These are a few of many examples that could be provided to show the development of the radiation curing coatings market. These polymer systems are widely used in the coatings as well as biomaterials industries [Berchtold et al., 2001]. On the kinetics of photopolymerization, particular behaviors are observed such as autoacceleration at the initial stage of reaction and autodeacceleration at the later stage of reaction, limited functional group conversion, delay in volume shrinkage with respect to equilibrium, unequal functional group reactivity, and propagation and termination reactions controlled by diffusion [Lecamp et al., 1997, 1999; Anseth et al., 1994; Cook, 1992]. In order to modify and control the final polymeric material properties, a better understanding of the kinetic behavior of the multifunctional acrylate systems is required.

The polymerization rate increases dramatically due to the diffusion controlled termination process in the initial stage of the reaction, which leads to autoacceleration. As the reaction progresses, the propagation reaction also becomes diffusion limited and the polymerization rate decreases in an autodeceleration mode [Lecamp et al., 1997]. The termination process becomes reaction diffusion controlled as termination by segmental movement of the macroradicals eventually becomes suppressed. The most facile termination reaction occurs between two relatively short chains whereas two longer entangled chains exhibit the slowest termination rate. Linear chains of various lengths have different mobility restrictions and effect on a termination kinetic parameter. Entangled chains of various lengths have different mobility restrictions as well. This termination mechanism is physically different from the termination mechanism by segmental or transitional diffusion, which implies the diffusion of macroradicals and chain segments to move radicals within a reaction zone before termination. For linear radical polymerization, the termination kinetic parameters as a function of chain length have been determined and included in the governing equations.

The classical kinetic model is based on the reaction equations of initiation, propagation and a bimolecular termination [Lecamp et al., 1999]. This mechanistic model assumes that reaction diffusion controlled termination dominates in the reaction. Because of the complex nature of the photopolymerization, typically in the termination process, the mechanistic model can be applied to the crosslinking radical polymerization only at the very early stage of the reaction. In a few works, the autocatalytic model has been used to analyze the multifunctional radical polymerization of (meth)acrylate macromonomers. Basically, this phenomenological model, which was widely used to study cure reactions of thermosetting resins, includes two kinetic relations: the n-th order reaction and autocatalytic reaction.

The formation of interpenetrating polymer networks (IPNs) via photopolymerization is also one of the key subjects of current researches in the coating industries. IPNs are related to other multicomponent polymeric materials such as polymer blends, grafts and blocks, but have the advantage of crosslinking, which allows exceptional control of morphology. The formation of IPNs via photopolymerization offers a great promise for the future in a view of the increasing number of applications of IPN materials in the coating industries [Li et al., 2000; Hua et al., 1999; Decker et al., 1995, 2001].

In the present study, the photopolymerization of thermoplastic polyurethane/acrylate blends is characterized in terms of kinetics and morphology. A modified mechanistic model with a diffusion

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control factor term will be introduced to characterize the photopolymerization of thermoplastic polyurethane/acrylate blends.

## EXPERIMENTAL

### 1. Materials

Thermoplastic polyurethane (TPU) with an $M_n$ of $1.5\times10^5$ g/mol, consisting of alternating 4,4′-methylene-diphenyldiisocyanate (MDI) and 1,4-butane diol (BD) was supplied by KOLON Chemical (K-480PNAT). As an acrylate macromonomer, poly(ethylene glycol) dimethacrylate (M=330, 550, 875 g/mol, Aldrich) was used as received. The trimethylol propane triacrylate (TMPTA, Aldrich) was added to control the functionality and viscosity of the mixture. The chemical formula of the reactants used is shown in Fig. 1.

### 2. Preparation of Films

The photoinitiator 1-hydroxy cyclohexyl phenyl ketone (Ciba Geigy, Darocur 184C) was dissolved in the mixture of these components under stirring at room temperature and then temperature increased up to reaction temperature under light cover. The photoinitiator concentration was fixed and the relative amounts of the other products were changed according to experimental conditions. Formulations were cast on the glass plates using an applicator with a gap of 52 μm. Samples were irradiated with a medium pressure mercury lamp (465 mW/$cm^2$) at 60 °C.

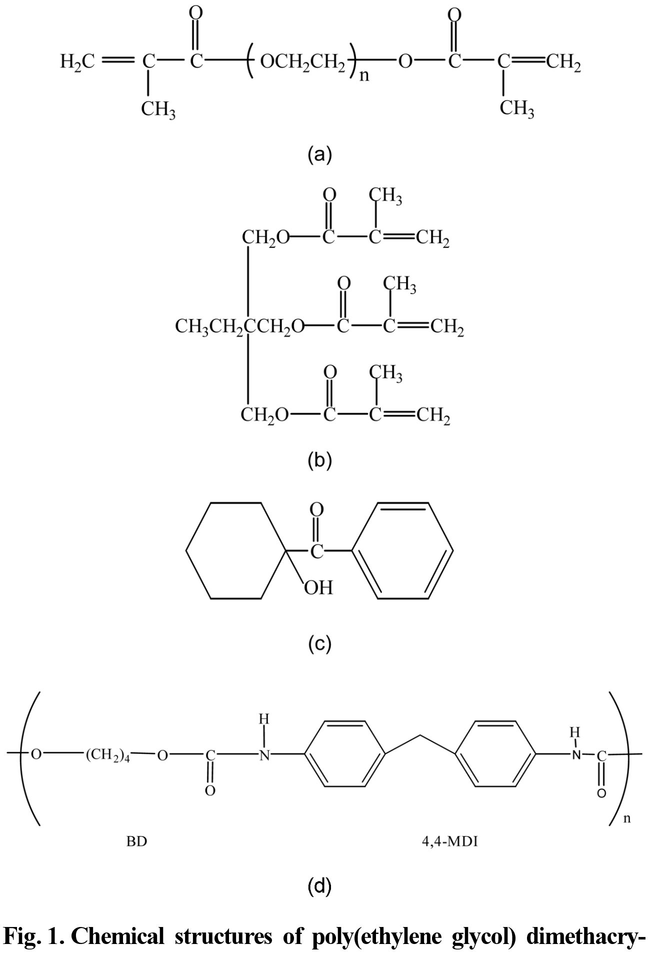


Fig. 1. Chemical structures of poly(ethylene glycol) dimethacrylate (a), trimethylol propane triacrylate (b), 1-hydroxy cyclohexyl phenyl ketone (c), and thermoplastic polyurethane (d).

### 3. Real Time - Fourier Transform Infrared Spectroscopy (RT-FTIR)

Real time - Fourier transform infrared spectroscopy (RT-FTIR) (ReatIR 1000 spectrometer) was used to measure reaction conversion versus reaction time. An uncured mixture was placed on the compartment of an RT-FTIR where it was exposed to the UV radiation of a metalhalide lamp of 465 W/$cm^2$ light intensity. In some experiments a thin glass slide was laminated on the top of the uncured resin to prevent the diffusion of oxygen. The polymerization of the sample exposed to both the excitation UV beam and the analysis IR beam was followed by RT- FTIR spectroscopy.

As the polymerization reaction starts, the acrylate double bonds (C=C) are to be consumed and the reaction usually stops because of the complete consumption of the acrylate double bonds. The disappearance of the peak of the acrylate double bonds was continuously monitored every 0.2 second. The C=C stretching vibration of the acrylate functional groups at 1,637-1,638 $cm^{-1}$ was used to calculate reaction conversions [Lecamp et al., 2001].

### 4. Morphology

Scanning electron microscopy (SEM) was used to characterize the morphology of IPNs. These specimens were prepared at 60 °C for 30 seconds. Then, their fractured surfaces were etched by dimethyl formamide (DMF) for 24 hrs in the stirred reactors in order to wash out the phase-separated thermoplastics from the fractured surfaces and then to clearly see the phase-separated regime. Finally, the surface was coated gold vapor before examining.

## RESULTS AND DISCUSSION

### 1. Reaction Conversion

The photopolymerization kinetics was studied by using RT-FTIR. The polymerization temperature maintained at 60 °C since photopolymerization is known to evolve an important thermal effect and kinetic constants are very sensitive to an increase in temperature. The reaction usually stopped because of the complete consumption of the acrylate double bonds. The C=C stretching vibration of the acrylate functional group at 1,637-1,638 $cm^{-1}$ was used to calculate reaction conversions. After the baseline is adjusted, the conversion of the acrylate functional group can be calculated by mea-

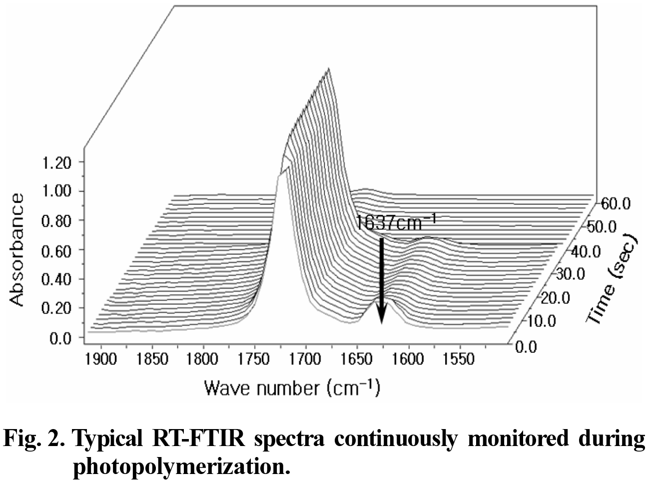


Fig. 2. Typical RT-FTIR spectra continuously monitored during photopolymerization.

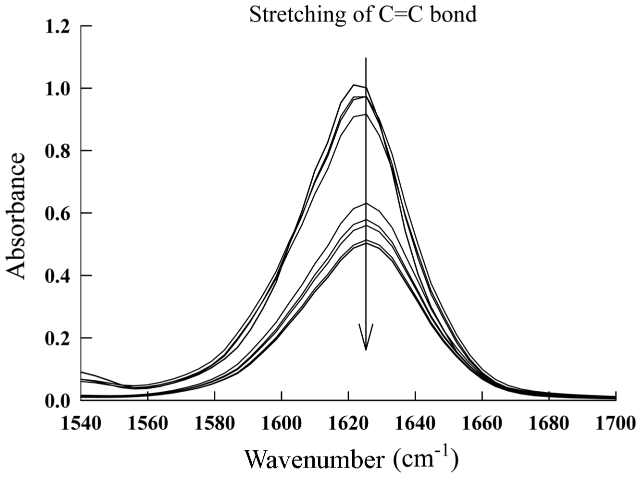


**Fig. 3. Typical decay of the stretching vibration bands of dimethacrylate double bonds at 1,638 cm$^{-1}$ (time interval=0.2 sec).**

suring at each time of the reaction and determined as follows [Lecamp et al., 2001]:

$$\alpha_{c=c(t)} = \frac{A_0 - A_t}{A_0} \times 100 \tag{1}$$

where $\alpha(t)$ is the conversion of the reactive function at time t, $A_0$, the initial absorbance and $A_t$, the absorbance of the function group at time t. RT-FTIR spectra continuously monitored during photopolymerization and a typical decay of the stretching vibration bands of acrylate double bond at 1,637-1,638 cm$^{-1}$ are shown in Fig. 2 and Fig. 3, respectively. It is usually observed that the higher the reaction rate, the higher the free volume, leading to a higher final reaction conversion of the material.

## 2. Mechanistic Model with Diffusion Control Factor

The model is based on the classical chemical equations of initiation and propagation, and assumes a bimolecular termination:

Initiation

$$A_2 \xrightarrow{h\nu} 2A^\bullet \qquad R_i = 2.3\phi\varepsilon I_0[A_2] \tag{2}$$

$$A^\bullet + M \longrightarrow AM^\bullet \qquad [A_2] = [A_2]_0 e^{-2.3\phi_0\varepsilon I_0 t} \tag{3}$$

Propagation:

$$-M^\bullet + M \xrightarrow{k_p} -MM^\bullet \qquad R_p = -\frac{d[M]}{dt} = k_p[M^\bullet][M] \tag{4}$$

Bimolecular termination:

$$-M^\bullet + {}^\bullet M- \xrightarrow{k_t} -MM- \qquad R_t = -\frac{d[M^\bullet]}{dt} = 2k_t[M^\bullet]^2 \tag{5}$$

where $R_i$, $R_p$, $R_t$ are respectively the initiation, propagation and termination rates, $k_p$ and $k_t$ are, respectively, the propagation and termination rate constants, $\phi$ is the initiation quantum yield, $\phi_0$ is the number of radicals produced per absorbed light energetic quanta, $\varepsilon$ is the molar extinction coefficient, $I_0$ is the light intensity, $[A_2]$ and $[M]$ are respectively the photoinitiator and monomer concentrations. At low photoinitiator concentration and assuming a quasi-steady state for $[M^\bullet]$, the propagation rate can be expressed by:

$$R_p = \frac{k_p}{k_t^{1/2}}[M]\sqrt{\frac{2.3\phi\varepsilon I_0[A_2]}{2}} \tag{6}$$

As this analysis, however, assumes that the average values of kinetic rate constants do not vary during the reaction time, the change of apparent kinetic rate constants during the reaction time cannot be described by this analysis. The change in apparent kinetic rate constants should be reflected in the reaction rate expression. In general, termination is controlled by polymer diffusion, whereas propagation is controlled by small monomer molecules. At the beginning of the reaction, the diffusion coefficient of the species decreases with the increase in double bond conversion and explains the rapid drop of apparent kinetic constants even keeping the same reactivity of all the double bonds.

A reaction rate equation with a diffusion control factor is a semi-empirical equation based on free-volume considerations [Chern et al., 1987; Khanna et al., 1993; Choe et al., 2003], and it has been proposed to explain the retardation of radical/cationic crosslinking reaction in the later stage of the reaction. Due to the gelation of acrylate macromonomer, the later stage of the reaction is virtually subjected to diffusion control. The diffusion-controlled rate constant $k_d$ is as follows:

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{7}$$

and

$$k_c = \frac{k_p}{k_t^{1/2}}\sqrt{\frac{2.3\phi\varepsilon I_0[A_2]}{2}} \tag{8}$$

where $k_c$ is the rate constant for chemical kinetics, C is a parameter of diffusion control, and $\alpha_c$ is a critical value of reaction conversion. In Eq. (7), as a reaches $\alpha_c$, the cure reaction becomes controlled by diffusion. The diffusion control factor, $f(\alpha)$ can be expressed as follows:

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{9}$$

where $k_e$ is an effective rate constant which is given by the following equation:

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{10}$$

Finally, the predicted kinetic rate expression can be written as

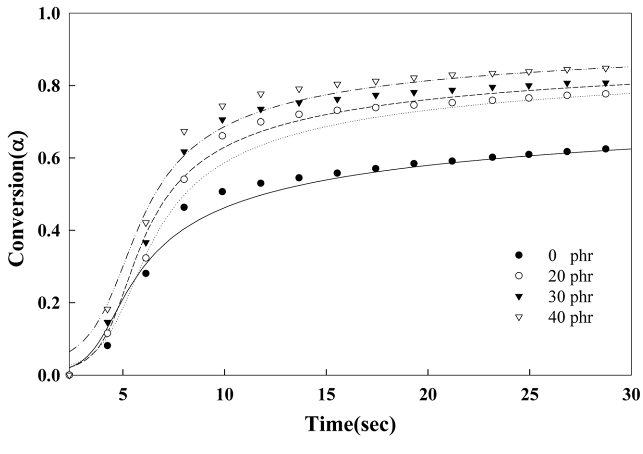


**Fig. 4. Model predictions using a modified mechanistic rate model with a diffusion control factor term.**

$$R_p = \frac{k_e(1-\alpha)}{1+\exp[C(\alpha-\alpha_c)]} \tag{11}$$

Autocatalytic nature of crosslinking reaction, characterized by the maximum polymerization rate at the early stage of the reaction, is clearly shown from the start of the reaction. In Fig. 4, all the dashed and solid lines, based on the calculation using the predicted kinetic rate expression, i.e., the modified mechanistic model, fit the experimental data in the whole range of reaction during the period of reaction time.

The ultimate conversion also increases due to the greater mobility of the small molecules leading to faster reaction diffusion and faster transfer of the radical species through the unreacted functional groups; eventually, as a termination mechanism the radical species encounter a second radical for a termination step. The conversion drastically increased as time increased, as was also seen in some works on kinetics of acrylate photopolymerization. After a drastic increase in conversion in the early stages of the reaction, a retardation of the reaction conversion occurred gradually as the polymer matrix became vitrified and the reaction rapidly became diffusion controlled. The polymerization rate curves were autocatalytic in nature, with the maximum rate of conversion at the initial stage of reaction, which is similar in behavior with that of other acrylate systems. As the polymerization rate increased, the position of the maximum rate of conversion was shifted to the start of the reaction.

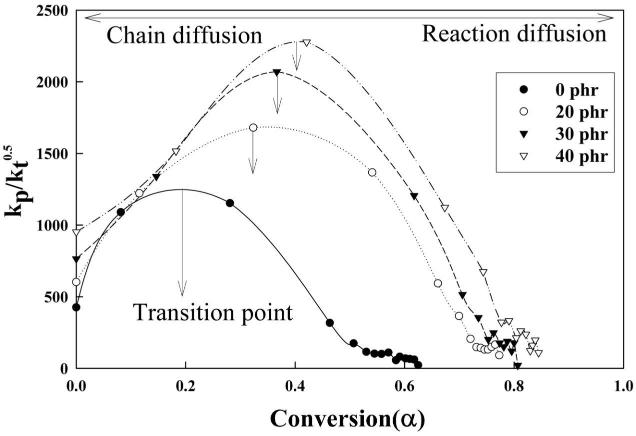
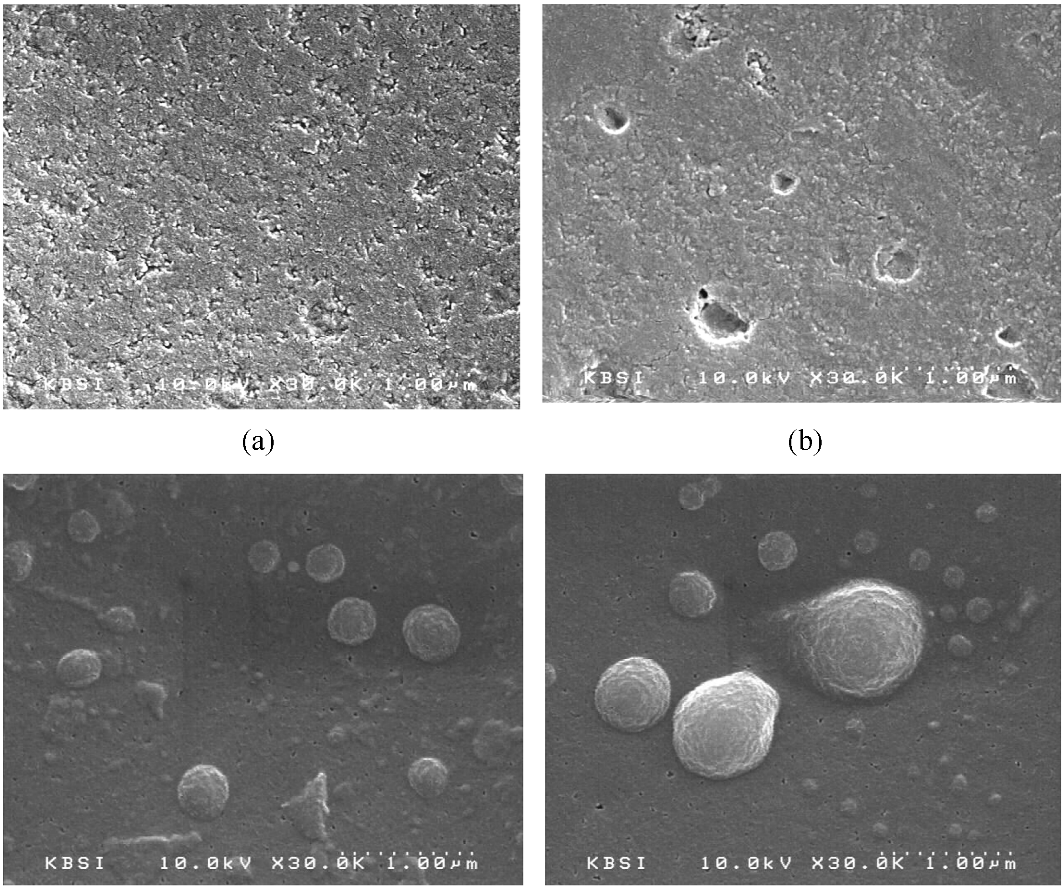


**Fig. 5. Determination of chain and reaction diffusion region of the photopolymerization reaction.**

**3. Determination of Propagation and Termination Rate Constants**

It is well known that the termination step is under diffusion control through the entire polymerization, but the dominant diffusion mechanism changes from segmental/translational chain diffusion



(a) (b)

(c) (d)

**Fig. 6. SEM images photopolymerized TPU/acrylate blends (0 phr (a), 20 phr (b), 30 phr (c), and 40 phr (d) of TPU).**

to reaction diffusion as the polymerization proceeds. In Eq. (8), the transition point is placed at the maximum value of $k_p/k_t^{0.5}$ in the rate expression. The calculated values of $k_p/k_t^{0.5}$ are plotted in Fig. 5. As the content of TPU increased, the location of the transition point appeared at higher value of reaction conversion. This indicates that as the content of TPU increases, reaction diffusion begins to dominate relatively in the later stage of the polymerization. Without TPU in the system, chain reaction dominates only in the early stage of the polymerization.

### 4. Miscibility of Uncured Thermoplastic Polyurethane/Acrylate Blends

The clouding behavior of the uncured thermoplastic polyurethane/acrylate blends was observed to investigate the miscibility of the uncured blends by increasing temperature up to 120 °C on the hot plate. All the uncured thermoplastic polyurethane/acrylate blends were optically clear and no phase separation was observed as increasing temperature up to 120 °C. In the range of 5 to 30 phr of TPU, the photopolymerized films were optically clear and obviously could be used as coating materials. But, over 40 phr of TPU there was a big in optical transparency due to the phase separation, which was clearly shown in SEM images in the following discussion.

### 5. Morphology of Photopolymerized Blends

According to the SEM images of prepared films containing 0 to 40 phr of TPU, as shown in Fig. 6, phase separation was not observed up to 20 phr of TPU. Over 30 phr of TPU, there was phase separation and so it began to be optically unclear. At 40 phr of TPU phase separation was clearly observed. Morphological investigation is very important to modify the polymeric films by means of the formation of IPNs and to apply them to the optically transparent films in the coating industries. In a view of this, phase separation behaviors must be considered to control the transparency of the films. For photopolymerized thermoplastic polyurethane/acrylate blends, TPU content is allowed up to 20 phr to make them transparent.

For all IPNs formed in the present study, the domains should be mainly formed by TPU network, and the acrylate network exists as matrix in the IPNs. It is found that the contents of the TPU in the IPNs rarely influence the induction period, and the photopolymerization rate changes a little at the early stage of the reaction. Thus, it can be said that the fast formation of such an IPN should give rise to phase separation of the system at earlier stages so as to greatly suppress the early step diffusion of TPU into acrylate domains as consistently with the SEM images clearly showing the phase separation specially at higher contents of TPU in IPNs.

## CONCLUSIONS

The photopolymerization rate curves of thermoplastic polyurethane/acrylate blends were autocatalytic in nature at the initial stage of reaction and a kinetic rate equation with a diffusion control factor term fit the experimental data. As the reaction conversion reaches the transition point, at which the maximum value of $k_p/k_t^{0.5}$ in the rate expression is obtained, the reaction becomes to be controlled by diffusion due to the restricted mobility of acrylate macromonomers. Interpenetrating polymer networks (IPNs) of thermoplastic polyurethane (TPU)/acrylate blends were formed in the limited range of TPU content in the formulations. As the content of thermoplastic polyurethane increased, the polymerization rate increased in the early stage of cure reaction. In the range of 5 to 30 phr of TPU, prepared films were optically clear. By the morphological investigation of the present IPNs, up to 20 phr of TPU is allowed to make them transparent and these IPNs can be used as coating materials.

## ACKNOWLEDGMENT

This work was supported by a grant from Pusan National University, by the Brain Korea 21 Project in 2005, and by grant No. R01-2005-000-10005-0 from the Basic research Program of the Korea Science & Engineering Foundation, South Korea.

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