Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

SYNTHESIS OF WATER-SOLUBLE URETHANE ACRYLATE CATIONOMERS AND THEIR ULTRAVIOLET COATING PROPERTIES

Jee-Hyun Ryu[a]; Jin-Woong Kim[a]; Kyung-Do Suh[a]
[a] Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul, Korea

To cite this Article Ryu, Jee-Hyun , Kim, Jin-Woong and Suh, Kyung-Do(1999) 'SYNTHESIS OF WATER-SOLUBLE URETHANE ACRYLATE CATIONOMERS AND THEIR ULTRAVIOLET COATING PROPERTIES', Journal of Macromolecular Science, Part A, 36: 4, 571 — 586

To link to this Article: DOI: 10.1081/MA-100101549

URL: http://dx.doi.org/10.1081/MA-100101549

J.M.S.—PURE APPL. CHEM., A36(4), pp. 571–586 (1999)

SYNTHESIS OF WATER-SOLUBLE URETHANE ACRYLATE CATIONOMERS AND THEIR ULTRAVIOLET COATING PROPERTIES

JEE-HYUN RYU, JIN-WOONG KIM, and KYUNG-DO SUH*

Division of Chemical Engineering
College of Engineering
Hanyang University
Seoul 133-791, Korea

Key Words: Water-Soluble Urethane Acrylate Cationomers, Ultraviolet (UV) Curing, Improved Coating Properties, Ionic Hard Domains, Glass Transition Peak T_{gh}, Positively-Charged

ABSTRACT

Water-soluble urethane acrylate cationomers were synthesized by incorporating N-methyldiethanolamine (MDEA) into the molecular backbone for an application of ultraviolet (UV) curing. It was found that they were easily dissolved in, because of the sufficient hydration ability of the incorporated cationic groups. Differing from conventional urethane acrylate derivatives, when UV-cured, the films of the urethane acrylate cationomers showed significantly improved coating properties. This was because of the formation of the ionic hard domains in the urethane acrylate network. In dynamic mechanical analysis (DMA), the formation of the ionic hard domain could be confirmed by detecting the glass transition peak T_{gh}, around 23.4°C. The dyeing of the urethane acrylate cationomer films was considerably favorable because of their positively-charged network structure.

---

* Author to whom correspondence should be addressed.

www.dekker.com

INTRODUCTION

Recently, waterborne coatings using ultraviolet (UV) curing technology have gained wide industrial interest, because they can decrease air pollution, reduce risks of fire, and improve aspects of occupational health and safety [1, 2]. In particular, odor, toxicity, the compromise between viscosity control and effects of the reactive diluent on the cured film properties and greater ease of cleaning are all reasons given for the possible use of water as a diluent in UV-curable system.

There are two types of water-based systems [1, 3]; emulsion or colloidal dispersion and water-soluble or dispersible. In the former case, usually, it is common practice to add surfactants to stabilize the emulsion or dispersion once it is formed [4-6]. They may assist the ease of formation of the emulsion and be a significant factor in controlling or determining the particle size of the resulting emulsion. Alternatively, however, some deterioration in performance has been observed due to the presence of these surfactants which remain in the cured film and which impart sensitivity to the finished coating. In the latter case, water-soluble or dispersible resins have been achieved by the incorporation of hydrophilic sites such as nonionic and ionic groups into the molecular backbone or end without adding surfactants [7-11]. Among hydrophilic sites, the incorporation of an ionic group has been more favored due mainly to the enhanced mechanical properties of the cured films. The ionic groups form an aggregate and act as a physical crosslinker, which is responsible for the marked improvement of the mechanical properties of the final films [12-16].

In our previous work [17], we synthesized water-soluble urethane acrylate cationomers containing N-methyldiethanol amine (MDEA) as a potential ionic site and polytetramethylene glycol (PTMG) as a soft segment in a molecule. Different from the conventional water-dispersible urethane acrylate derivatives, the urethane acrylate cationomers prepared in this study had a peculiar molecular structure; two ionic sites in a molecule. This was possible through a stepwise reaction procedure. With the help of this large ionic content in a molecule, they easily dissolved in water. So, these urethane acrylate cationomers were believed to have many advantages in material handling and compound preparation, as well as in diminishing the problem of air pollution in the field of UV curing.

The ultimate goal of this study was to synthesize water-soluble and UV curable urethane acrylate cationomers and to investigate their UV-coating properties. Isophorone diisocyanate (IPDI)-based urethane acrylate cationomers were synthesized with varying molecular weight of soft segments (PTMG) and degree of neutralization. The effects of the soft segment molecular weight, and the degree of neutralization on the coating properties were investigated.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, Mw=1.0(10^3 g(mol^{-1}, 1.4(10^3 g(mol^{-1}, and 2.0(10^3 g(mol^{-1}, Hyosung BASF), N-methyldiethanol-amine (MDEA, Aldrich Chemical Co.), glycolic acid (GA, Tokyo Kasei Organic Chemicals), and dibutyltindilaurate (DBTDL, Junsei Chemical Co.) were used as received. Inhibitors in 2-hydroxyethyl methacrylate (HEMA) were removed through a removing column (Aldrich Chemical Co.). N,N-dimethylacetamide (DMAc) was used as a solvent of MDEA and viscosity reducer after degassing at room temperature for 48 hours. Benzophenone (Janssen Chemical Co.) was used as a photoinitiator.

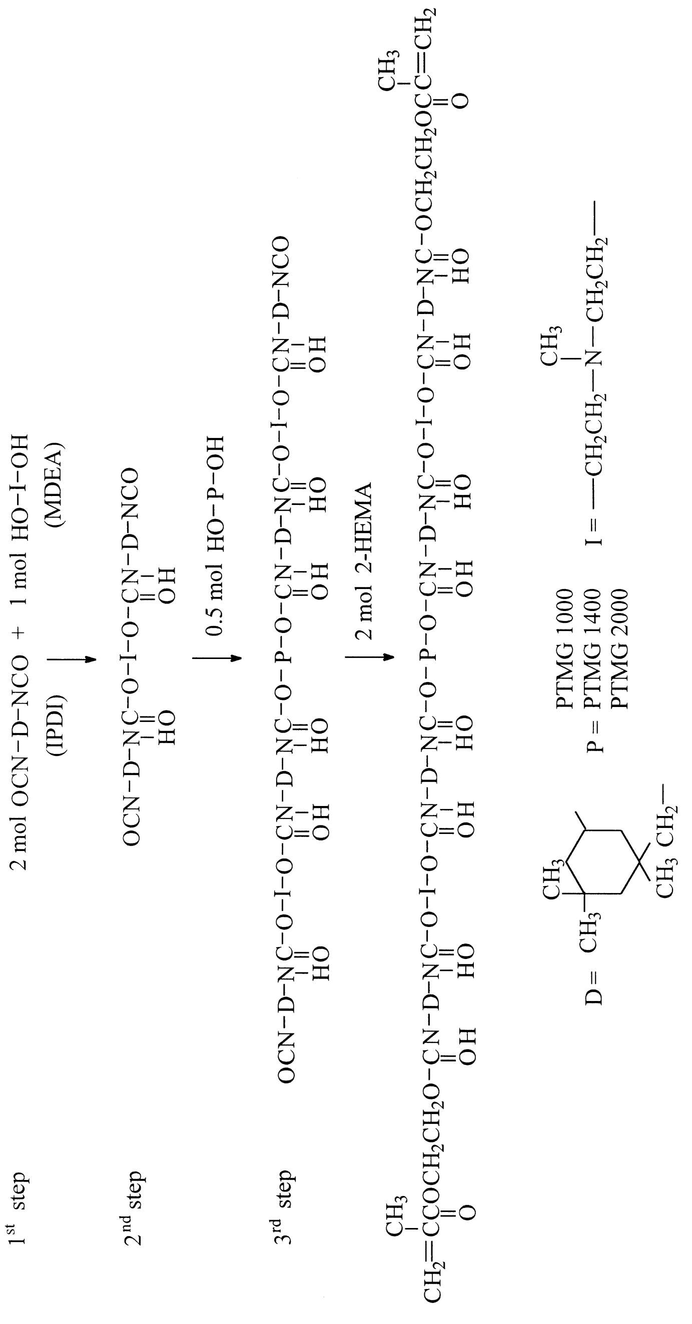
Synthesis of Urethane Acrylate Cationomers

Urethane acrylate cationomers were synthesized by a stepwise reaction procedure [17-19].

A schematic presentation for the reaction procedure and the molecular structure is shown in Scheme 1.

The synthesis was carried out in the 4-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. In the first step, IPDI containing 1 wt% of DBTDL was poured into the glass reactor after nitrogen gas inlet for 10 minutes to eliminate the residual moisture. MDEA dissolved in DMAc was dropped into the reactor slowly at 0°C. The reaction temperature was raised to 65°C so that 2 mole of IPDI reacted with the 1 mole of MDEA. In this stage, considerable care was given to control the molar ratio of the reaction, so as not to increase the molecular weight. This temperature was maintained for 3 hours to retain an acceptable rate of the reaction. The change of NCO value during the reaction was determined using dibutylamine back titration method to find out the end point of the reaction [20].

In the second step, 0.5 mole of PTMG was reacted with the same method



Scheme 1. The reaction procedure and schematic molecular structure of urethane acrylate cationomers with the molecular weight of the soft segment (PTMG).

as the first step. In the last step, after dissolving 1 wt% of DBTDL again, 2 mole of HEMA was reacted to the residual NCO groups at room temperature for 12 hours, capping both molecular ends with vinyl groups. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm^{-1}) through IR spectroscopy. Ingredients for the synthesis of urethane acrylate cationomers are listed in Table 1.

In order to purify DMAc, unreacted HEMA, and MDEA, the reaction mixture was precipitated from the water and filtered several times. The crude product was dried in a vacuum oven. Amine groups in cationomer were neutralized with the appropriate amount of GA at room temperature for 1 hour.

Preparation of Urethane Acrylate Cationomer Solution and Film

Ten grams of the urethane acrylate cationomer was placed in a beaker together with 3 wt% of benzophenone and stirred vigorously with a mechanical stirrer. Then, 30 g of the deionized water were dropped slowly.

Solutions prepared were poured into a polyethylene mold of which the inner dimension was 10 cm (10 cm (0.5 cm, and dried at 60°C for 24 hours *in*

TABLE 1. Ingredients Used for the Synthesis of Urethane Acrylate Cationomers[a]

Symbol	IPDI	MDEA	PTMG[b]			HEMA	GA	MDEA content (wt%)
			1.0×10^3	1.4×10^3	2.0×10^3			
IC1	50.00	13.40	56.23	-	-	14.58	8.55	9.39
IC1-88	50.00	13.40	56.23	-	-	14.58	7.53	9.39
IC1-75	50.00	13.40	56.23	-	-	14.58	6.41	9.39
IC2	50.00	13.40	-	78.72	-	14.58	8.55	8.11
IC3	50.00	13.40	-	-	112.46	14.58	8.55	6.73

[a] All units were represented in gram

[b] Molecular weight of polytetramethylene glycol (PTMG)

Abbreviation : IC means IPDI-based urethane acrylate cationomer. IC1, 2, and 3 correspond to ICs prepared with PTMG 1.0×10^3, 1.4×10^3, and 2.0×10^3, $g\cdot mol^{-1}$ respectively. IC1-88 and -75 are IC1 neutralized 88 and 75 %, respectively. Other samples were neutralized 100%.

vacuo. The dried urethane acrylate cationomers were cured with air irradiating static UV lamp (450 watt, UV lamp from Ace Glass Co.) for 5 minutes and postcured at 80°C for 5 hours. The films obtained were about 0.3 mm thick and stored in a desiccator at room temperature before testing.

Measurements

Molecular weight distributions were measured by a model 410 GPC equipped with Styragel HR 1-4 columns from Waters Associates at 25° C. The flow rate of the carrier solvent, THF, was 0.5 ml/min. The average molecular weights were calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standards. Resultant molecular weights for urethane acrylate cationomers are listed in Table 2.

The conversions were determined by measuring the gel fraction of various cured samples after extracting the unreacted materials in methylethyl ketone/acetone (4:6) mixture for 24 hours. Infra-red spectra were recorded using a Mahgna IR-550 of Nicolet Co.

Tensile properties were measured at 25°C using Instron (Model No. 4460) with a crosshead speed of 50 mm/min. All measurements respect the average of 5 runs. The dumbbell type specimen was 25 mm wide at two ends, 0.3 mm thick, and 6 mm wide at the neck.

Dynamic mechanical properties were obtained using DMA2980 (TA-instruments) at 2Hz. The cured films were quenched to -100°C and heated up to 100°C at 2°C/min. The sample chamber was kept drying by a stream of moisture-free nitrogen.

Pencil hardness, stain resistance, crosshatch adhesion, and flexibility test for the sample films were followed ASTM D 3363-92a, D 3023-87, D 3359-92a, and D 4145-83, respectively.

TABLE 2. Molecular Weights of Urethane Acrylate Cationomers

Symbol	Mw ($g \cdot mol^{-1}$)	Mn ($g \cdot mol^{-1}$)	PDI [a]
IC1	8.2×10^3	6.2×10^3	1.32
IC2	1.1×10^4	6.6×10^3	1.67
IC3	1.4×10^4	7.1×10^3	1.91

[a] Polydispersity index (PDI)

RESULTS AND DISCUSSION

The urethane acrylate cationomer has a peculiar molecular structure, as shown in Scheme 1. It has two vinyl groups enabled to crosslink each other at both ends and two ionic groups to hydrate in the molecular backbone. These ionic groups are expected to enhance the final coating properties by the ionic interaction. In addition, it also has a long polytetramethylene glycol (PTMG) soft segment in the middle of the molecule. By controlling the molecular weight of PTMG, the elastic property can be varied. Therefore, when UV-cured, the improved coating properties are expected, compared with conventional urethane acrylate derivatives.

UV-Curing Procedure

IR spectra taken before (a) and after (b) 5 minutes of UV irradiation and plotted to show the spectroscopic changes resulting from the curing process are shown in Figure 1. The disappearance of the C=C bond at 1638.01 cm^{-1} indicated that the vinyl polymerization reaction occurred.

Figure 2 shows the gel fraction of the urethane acrylate cationomers for a different molecular weight of the soft segment (PTMG) with the UV-irradiation time. As the molecular weight of soft segment increased, the polymerization rate became slower. This seemed to be attributed to the lower concentration of the vinyl groups. Within a 5 minute curing time, the samples were found to reach about 0.80 gel fraction. Under such results, it was reasonable to expect that the 5 minute-curing was suitable for preparation of the acrylate cationomer films.

Mechanical Properties of Urethane Acrylate Cationomer Films

Figure 3 shows the stress-strain curves of UV-coated films having a different molecular weight of the soft segment (IC1 (a), IC2 (b), and IC3 (c)). The maximum stress, the percent strain, and the initial modulus are summarized in Table 3. IC1 film having the lowest molecular weight of the soft segment exhibited the highest initial modulus and maximum stress and the lowest percent strain. On the contrary, as the molecular weight of the soft segment increased, the maximum stress and the initial modulus decreased and the percent strain increased. This trend was in good agreement with the work of W. Oraby *et al.* [21]. However, for the urethane acrylate cationomer films, it is notable that the maximum stress was much higher than those in the literature [2, 10, 11] (generally, the maximum stress of the conventional urethane acrylate films prepared

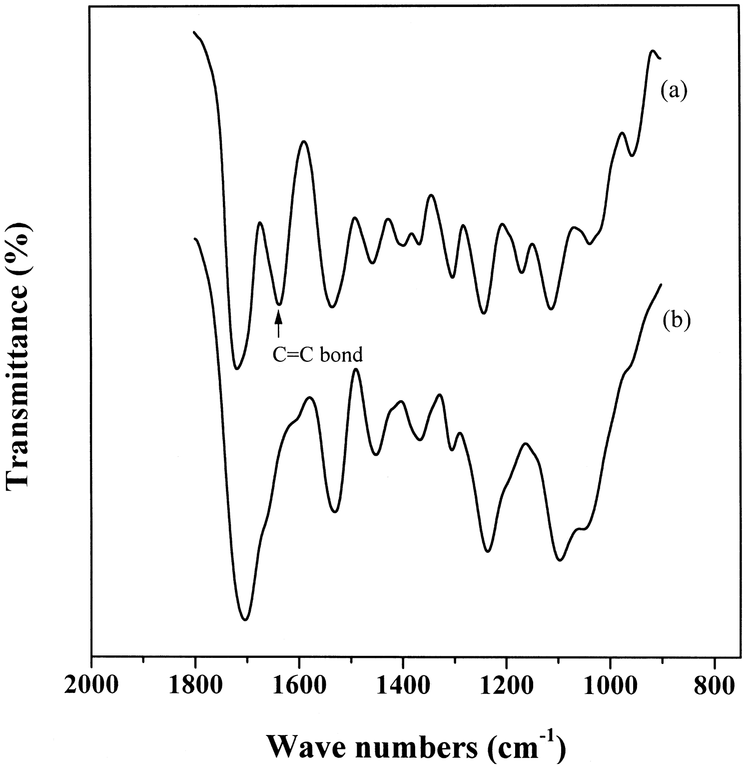


Figure 1. IR-spectra of IC1 before (a) and after (b) 5-minute UV-irradiation.

without using a reactive diluent was in the order of 2 ~10MPa). This suggests a synergistic effect on the coating properties by means of the incorporation of ionic groups into the network.

From the fact that IC1 having more ionic groups exhibited a high value of maximum stress, we assumed that the phase separation between the ionic hard segment domain and the polyether soft segment domain improved tensile properties. This could be confirmed by the dynamic mechanical analysis. The temperature dependence of storage modulus and loss modulus for IC1, IC2, and IC3 is shown in Figure 4. Two transition peaks for IC1 film were detected around –69.0°C and 23.4°C, corresponding to the glass transition temperature of the polyether soft segment domain, T_{gs}, and the ionic hard segment domain, T_{gh}, respectively. This result confirms that IC films were composed of two phases, the polyether soft segment domain and the ionic hard segment domain due to the difference in polarity between the ionic groups and the network [12-14]. Therefore, the ionic hard segment domain acted as a reinforcing filler in the ure-

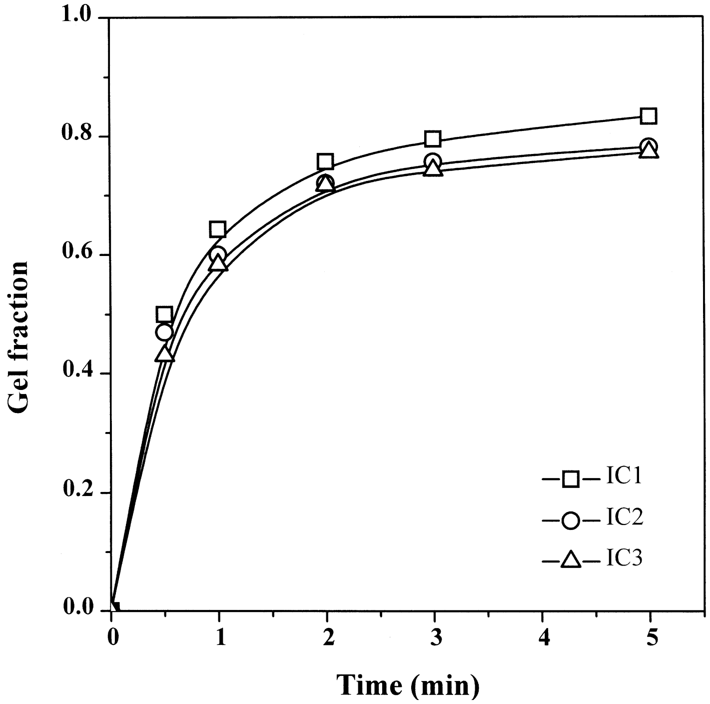


Figure 2. Gel fraction of urethane acrylate cationomers for the different molecular weight of the soft segments (PTMG) with the UV-irradiation time: IC1 (-□-), IC2 (-O-), and IC3 (-Δ-).

thane acrylate network, resulting in the enhancement of the maximum stress and the initial modulus, as shown in Figure 3. However, as the molecular weight of soft segment increased, the magnitude of T_{gh} decreased. It was believed that the degree of phase separation of the ionic hard segment domain from the network was reduced due to the reduction of the charge density, as listed in Table 1. The reduced phase separation of IC2 and IC3 films accompanied with lowering of the maximum stress and the initial modulus.

In order to confirm the effect of the phase separation induced by the ionic group incorporation on the coating properties in detail, IC1 films having a different degree of neutralization were prepared. Figure 5 shows the contact angle with the degree of neutralization of IC1 films. The degree of neutralization could be successfully certified by observing the drastic decrease of the contact angle of IC1 films with the degree of neutralization. Figure 6 shows the stress-strain curves obtained from IC1 films having the different degree of the neutralization. The results were also summarized in Table 3. As shown in Table

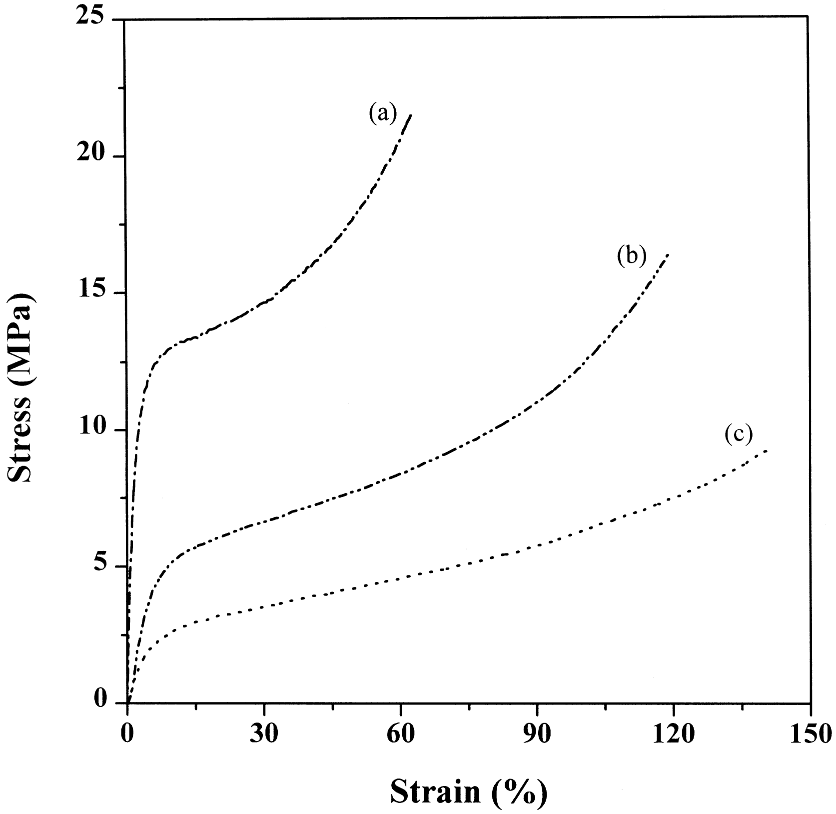


Figure 3. Stress-strain curves for the urethane acrylate cationomer films with the molecular weight of the soft segments (PTMG): IC1 (a), IC2 (b), and IC3 (c).

TABLE 3. Tensile Properties of UV-Cured Urethane Acrylate Cationomer Films

Symbol	Maximum stress (MPa)	Percent strain (%)	Initial modulus (MPa)
IC1	21.45	62.75	369.63
IC1-88	18.37	36.60	343.40
IC1-75	14.94	36.42	252.40
IC2	16.34	119.10	88.01
IC3	9.99	140.80	28.22

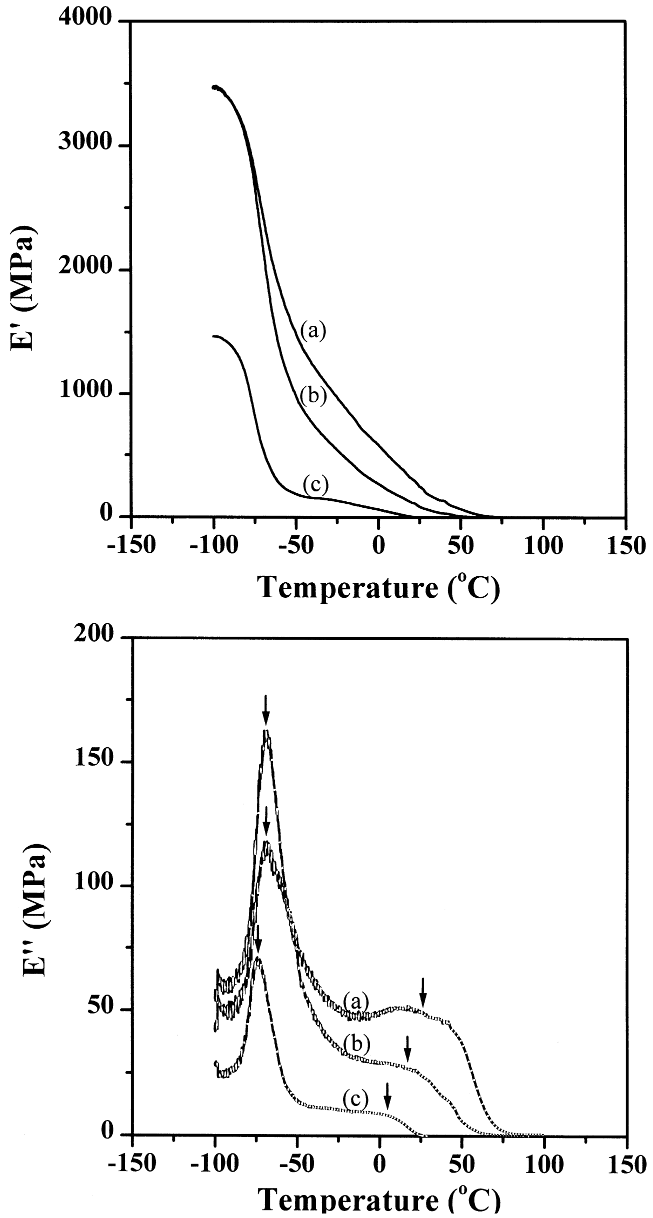


Figure 4. Dynamic mechanical analysis for IC1 (a), IC2 (b), and IC3 (c): dependence of storage modulus (EN) and loss modulus (EO) on temperature.

3, the maximum stress, percent strain, and initial modulus increased with the increase of the degree of neutralization. The dynamic mechanical properties of IC1 films with the degree of neutralization are shown in Figure 7. As the degree of neutralization decreased, the magnitude of T_{gh} peak gradually disappeared.

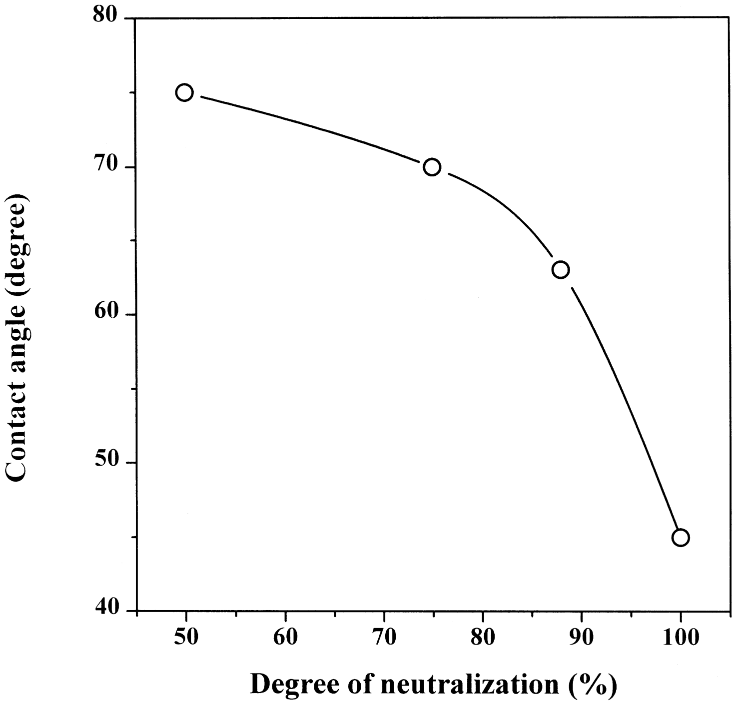


Figure 5. Contact angle with the degree of neutralization for IC1 film. 1 m1 of DDI water was dropped and contact angle was read using Erma contact angle meter, model G-1.

This result verifies that the incorporation of the ionic groups into the network induced the phase separation. Therefore, the enhancement in the coating properties could be achieved for the urethane acrylate cationomer films.

Other Coating Properties

Other coating properties of the urethane acrylate cationomer films are given in Table 4. Adhesion was measured using the crosshatch adhesion method. All films showed good adhesion. This result was due to the formation of grafting bond between PVC substrate and urethane acrylate groups of the multifunctional acrylates, which were initiated by the photoinitiator [10, 11]. Pencil hardness showed constant good results with 6H, which is attributed to the hard network structure formed by the phase separation of ionic groups from the urethane acrylate network, as illustrated above, as well as the high crosslinking density of the cured film. In the flexibility test, we could not observe any crack generation. This

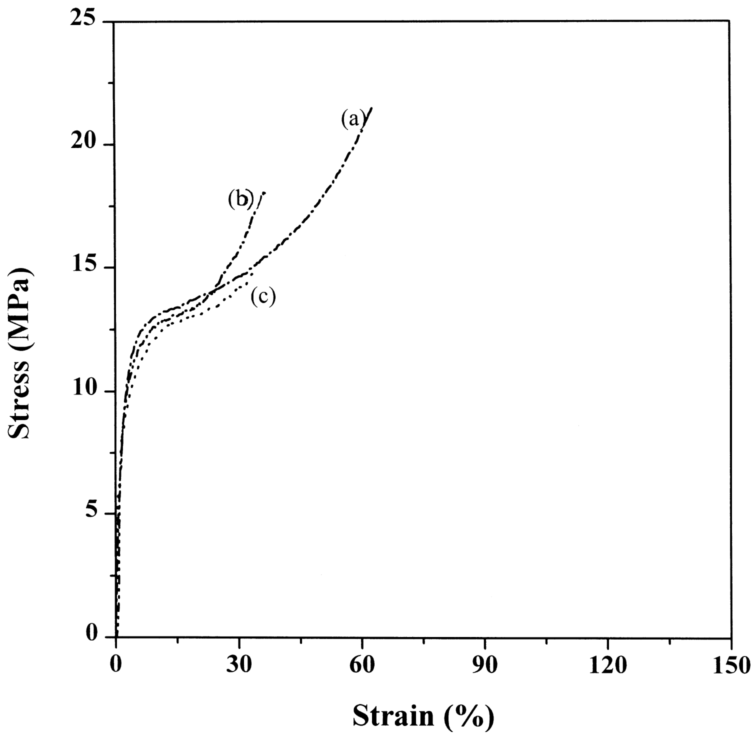


Figure 6. Stress-strain curve for IC1 film with the degree of neutralization: 100% (a), 88% (b), and 75% (c).

was interpreted by the flexible network formation due to the incorporated polyether soft segment. In the stain resistance test, the urethane acrylate cationomer films showed the poor results. Especially, IC1 film absorbed a large amount of a dye. It can be said that the urethane acrylate cationomer films had a good dying property because of the positive-charged network structure. In addition, the dyeing property was improved as the ion content increased.

CONCLUSION

Water-soluble and UV-curable urethane acrylate cationomers could be synthesized by incorporating MDEA into the urethane acrylate molecular backbone. The maximum stress of the urethane acrylate cationomer films was enhanced due to the phase separation induced by the ionic aggregate acting as a reinforcing filler in the network. These ionic aggregates could be confirmed by

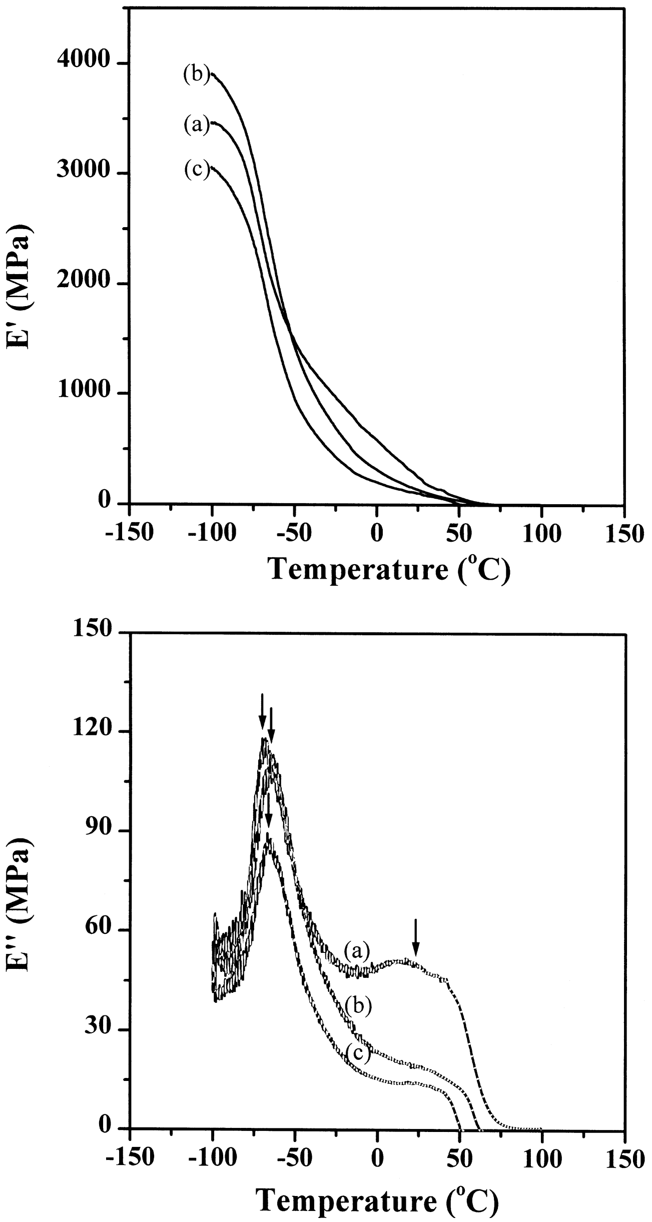


Figure 7. Dynamic mechanical analysis for IC1 film with the degree of neutralization: 100% (a), 88% (b) and 75% (c): dependence of storage modulus (EN), and loss modulus (EO) on temperature.

TABLE 4. General UV-Coating Properties of Urethane Acrylate Films

Item	IC1	IC2	IC3
Adhesion (/100)	100	100	100
Pencil hardness	6H	6H	6H
Flexibility (in.)	0	0	0
Stain resistance	Bad	Regular	Regular

observing the dynamic mechanical analysis, which displayed two transition peaks, the glass transition peak for the polyether soft segment domain, T_{gs}, and for the ionic hard domain, T_{gh}. Pencil hardness, adhesion, and flexibility of urethane acrylate cationomer films were measured and showed excellent results. Since the urethane acrylate cationomers and their films had an ability to absorb the dyes, further studies relative to the field of dyeing industries was possible.

ACKNOWLEDGEMENTS

J-H Ryu and J-W Kim are grateful to the Graduate School of Advanced Materials and Chemical Engineering at the Hanyang University for a fellowship. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998.

REFERENCES

[1] P. K. T. Oldring, *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*, Vol. 2, 1990.
[2] E. Hoyle and J. F. Kinstle, *Radiation Curing of Polymeric Materials*, ACS, Texas, 1989.
[3] J. M. Loutz, W. Demateau, and P. Y. Herze, *Water-based UV Coating System*, Radcure Europe ‘87 Conference.
[4] P. Sherman, *Emulsion Science*, Academic Press, 1968.

[5] P. Becher, *Emulsion-Theory and Practice*, ACS, Monograph 135, Reinhold Pub. Co., 1957.
[6] J. W. Kim, J. Y. Kim, and K. D. Suh, *Polym. Bulletin*, *36,* 141 (1996).
[7] S. A. Chen and J. S. Hsu, *Polymer, 34,* 2769 (1993).
[8] S. A. Chen and W. C. Chan*, J. Polym. Sci., Polym. Phys., 28*, 1499 (1990).
[9] J. Y. Kim and K. D. Suh, *Macromol. Chem. Phys., 197*, 2429 (1996).
[10] M. O. Song, J. Y. Kim, and K. D. Suh, *J. Coating Technology, 68,* 43 (1996).
[11] M. O. Song, J. Y. Kim, and K. D. Suh, *J. Appl. Polym. Sci., 62***,** 1775 (1996).
[12] C. Z. Yang, T. G. Grasel, J. L. Bell, R. A. Register, and S. L. Cooper, *J. Polym. Sci., Polym. Phys., 29,* 581 (1991).
[13] T. A. Spechard, K. K. S. Hwang, S. B. Lin, S. Y. Tsay, M. Koshiba, Y. S. Ding, and S. L. Cooper, *J. Appl. Polym. Sci., 30,* 647 (1985).
[14] M. R. Tant, K. A. Mauritz, and G. L. Wilkes*, Ionomers; Synthesis, Structure, Properties, and Application*, Champman & Hall, 1997.
[15] B. K. Kim, K. H. Lee, and N. J. Jo, *J. Polym. Sci., Polym. Chem., 34,* 2095 (1996).
[16] B. K. Kim, *Colloid Polym. Sci., 274,* 599 (1996).
[17] J. W. Kim and K. D. Suh, *J. Mac. Sci., Pure & Appl. Chem., A35 (9),* 157 (1998).
[18] J. W. Kim and K. D. Suh, *J. Appl. Polym. Sci., 69*, 1079 (1998).
[19] J. W. Kim and K. D. Suh, *Colloid Polym. Sci., 276*, 342 (1998).
[20] J. David and H. B. Staley, “Analytical Chemistry of Polyurethane”, High Polymer Series, XVI, Part III, Wiley-Interscience, New York, 1969.
[21] W. Oraby and W. K. Walsh, *J. Appl. Polym. Sci., 23***,** 3227 (1979).

Received May 20, 1998
Revision received December 10, 1998

Downloaded At: 13:26 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081MA100101549