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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Kim, Jin-Woong and Suh, Kyung-Do(1998) 'Viscosity Properties for Aqueous Solution of Urethane Acrylate Cationomer', Journal of Macromolecular Science, Part A, 35: 9, 1587 – 1601

To link to this Article: DOI: 10.1080/10601329808007318

URL: <http://dx.doi.org/10.1080/10601329808007318>

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VISCOSITY PROPERTIES FOR AQUEOUS SOLUTION OF URETHANE ACRYLATE CATIONOMER

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ABSTRACT

Water-soluble and UV-curable urethane acrylate cationomer was synthesized incorporating N-methyldiethanol amine (MDEA) on the molecular backbone and its viscosity properties were examined with respect to shear rate, temperature, and weight fraction of resin. All shear rates showed shear rate independence within given fraction regions. The viscosity trends of urethane acrylate cationomer solutions followed the Arrhenius equation well. The logarithmic infinite viscosity and activation energy showed linear relationship with the fraction below the weight fraction of 0.325. However, above the fraction of 0.325, the deviation from linear relationship was observed. This was believed to be attributed to the intermolecular interactions among molecular chains. From the obtained linear correlation of the logarithmic infinite viscosity and activation energy with the fraction, rheological equation of state was proposed. The viscosities obtained from the equation of state successfully corresponded to the results of experiments.

INTRODUCTION

Waterborne coatings using ultraviolet (UV) curing technology have gained wide industrial interest because they can reduce air pollution, reduce fire risks, and improve aspects of occupational health and safety [1, 2]. A wide range of acrylate-

functional oligomer is available in order to meet the various application requirements; i.e., polyester acrylate, epoxy acrylate, urethane acrylate, and so on. In particular, urethane acrylate has gained industrial acceptance, because it imparts the toughness, abrasion resistance, and elastomeric properties inherent to polyurethane acrylate to the coating [3]. However, in many cases, high fraction of organic volatile compounds has been used to reduce the viscosity, resulting in serious pollution problems and diminution of coating properties of raw materials.

So far, water-dispersible resins have been prepared incorporating hydrophilic groups into molecular backbone for polymer and/or oligomer to improve water dispersibility. S. A. Chen *et al.* reported polyurethane ionomers by incorporating anionic or cationic group onto the molecular backbone [4, 5]. K. Noll patented aqueous dispersions of polyurethane having side chain polyoxyethylene units [6]. In our previous works [7-9], as a water-dispersible and UV-curable oligomer, we reported urethane acrylate having hydrophilic polyoxyethylene group in a side of the chain. However, few studies have been performed about water-soluble urethane acrylate species, even though strong requirements have been prevalent in various fields related to UV-curing technology.

The goal of this study is to prepare water-soluble urethane acrylate cationomer and investigate the viscosity properties in aqueous media prior to its application to UV-curing technology. Within the fraction region performing the UV-curing, the viscosity was also predicted using rheological equation of state as a function of fraction and temperature.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Junsei Chemical Co.) was vacuum distilled before use. Polytetramethylene glycol (PTMG, $M_w=1,000$, Hyosung BASF), N-methyldiethanol amine (MDEA, Aldrich Chemical Co.), glycolic acid (Tokyo Kasei Co.), and dibutyltindilaurate were used as received. Inhibitor in 2-hydroxyethyl methacrylate (2-HEMA) was removed through removing column (Aldrich Chemical Co.) and stored at 5°C. N,N-dimethylacetamide (DMAc) was used as a solvent of MDEA and viscosity reducer after degassing at room temperature for 48 hours.

Synthesis of Urethane Acrylate Cationomer

For the synthesis of MDEA-incorporated urethane acrylate cationomer (MUAC), the reaction was carried out in the four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and nitrogen gas inlet system. In

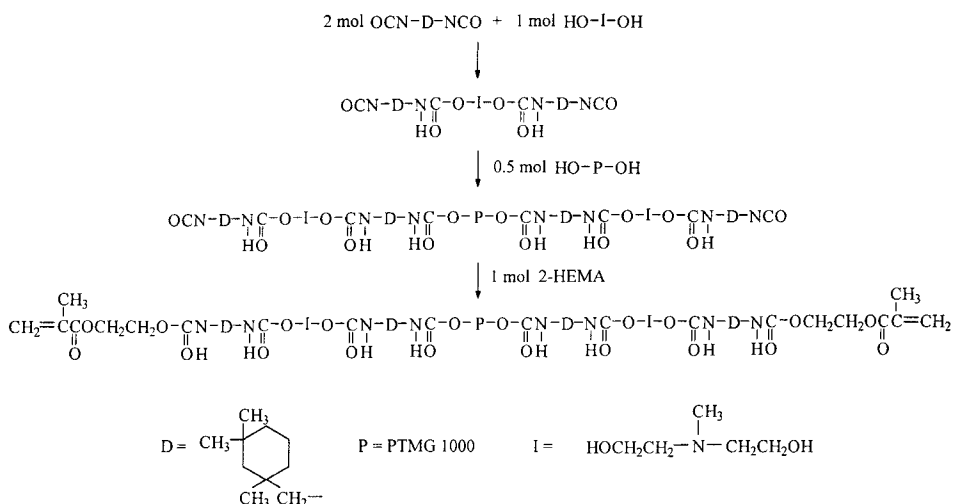


Figure 1. A model representation of urethane acrylate cationomer.

the first step, IPDI was poured into the glass reactor and nitrogen gas was inlet for 10 minutes to eliminate the residual moisture. After dissolving 1 wt% of dibutyltindilaurate, MDEA dissolved in DMAc was dropped into the reactor slowly at 0°C. Then, the reaction temperature was raised to 70°C so that 2 mol of IPDI reacted with the 1 mol of DMPA. In this stage, care must be taken of controlling the molar ratio of the reactants, so as not to increase the molecular weight. This temperature was maintained for 4 hours to retain an acceptable rate of reaction. The change of NCO value during reaction was determined using dibutylamine back titration method to find out the end point of the reaction [10].

In the second step, 0.5 mol of PTMG was added slowly into the reactor to incorporate soft segment into the molecular backbone with the same method of the first step and reacted for 4 hours at 70°C. In the last step, after dissolving 1 wt% dibutyltindilaurate into the reactor, 2-HEMA was reacted to the residual NCO group at 45°C for 12 hours. This procedure could make the molecular ends capped with vinyl group. The reaction end point was determined by the disappearance of NCO stretching peak (2270 cm⁻¹) through IR spectroscopy. The reaction procedure and molecular structure are shown in Figure 1. The ingredients used for the synthesis of MUAC and molecular weights of MUAC are summarized in Table 1.

To purify DMAc, unreacted 2-HEMA, and MDEA, the reaction mixture was precipitated from the water and filtered several times to give crude product. The

TABLE 1. Ingredients Used for the Synthesis of MUAC and Molecular Weights of MUAC

Ingredient	Weight (g)	
IPDI	50.00	
MDEA	13.40	
PTMG (M _w =1000)	56.23	
2-HEMA	14.64	
^a DMAc	89.51	
^b DBTDL	1.34	
^c GA	8.55	
Wt. Avg. Mw	No. Avg. Mw	Polydispersity index
8242	6244	1.32

^a N,N-dimethylacetamide : the resin content was fixed with 60 %

^b Dibutyltindilaurate

^c Glycolic acid

crude product was dried *in vacuo*. The amine group of MUAC was ionized with appropriate amount of glycolic acid at room temperature for 1 hour.

Figure 2 shows the proton and ¹³C-NMR of MUAC spectra recorded. For the cationic group in the molecule, proton NMR signals were as follow; $\delta = 2.55$ ppm (H_h) for methylene group of MDEA incorporated; $\delta = 2.21$ ppm (H_i) for methyl group of MDEA; other signals for typical protons of urethane acrylate. ¹³C-NMR signals were as follows; $\delta = 43.5$ ppm for carbon of methyl group attaching to nitrogen of MDEA; $\delta = 125.5$ and 136.0 ppm for carbons of vinyl group; $\delta = 171.6$ for carbon of urethane linkage. The above results suggest that the urethane acrylate incorporating cationic group into the molecular backbone was synthesized successfully.

Preparation of Urethane Acrylate Cationomer Solution

10 g of MUAC was placed in a beaker and stirred vigorously with a mechanical stirrer, and water was dropped continuously. With the added amount of water, the weight fraction of MUAC in water was controlled. To minimize the effect of pH, electrolyte, and dust particles on the viscosity of MUAC solution, distilled deionized water was used after filtering through sintered-glass filter.

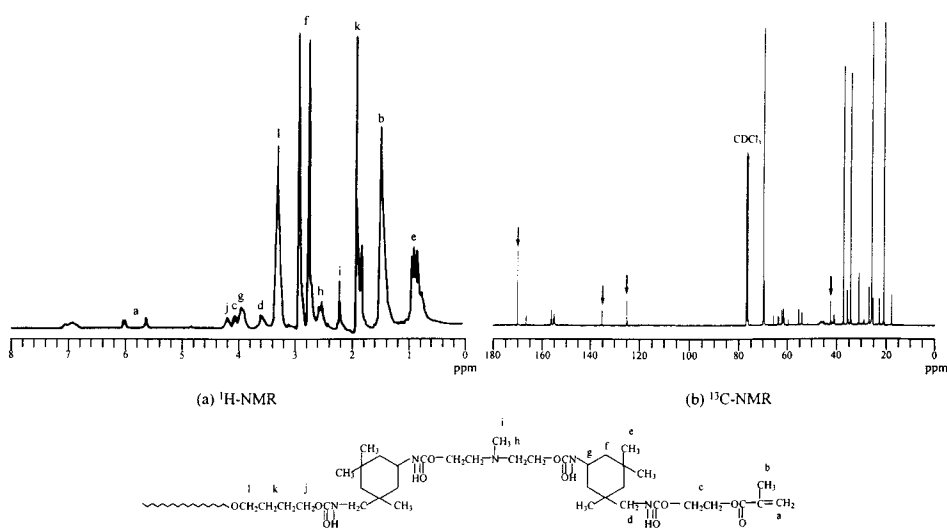


Figure 2. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra for urethane acrylate cationomer.

Measurements

The 200 MHz $^1\text{H-NMR}$ spectra were recorded with Varian Gemini spectrometer, and $^{13}\text{C-NMR}$ spectra were obtained on solutions in CDCl_3 using a JEOL GX400 spectrometer operating at 100 MHz for carbon. Chemical shifts were calculated relative to CDCl_3 : 77.0 ppm.

Molecular weight distributions of MUAC 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⁻¹.

The viscosity of MUAC solution was measured with the Brookfield Viscometer, Model RVRH. The temperature of the solution was varied from 10°C to 50°C with the accuracy of $\pm 0.1^\circ\text{C}$ in a thermostated bath. All viscosities were measured below 50°C, because the vinyl groups of MUAC molecular ends rendered to polymerize in the course of measuring viscosities. The shear rate varied from 0 sec⁻¹ to 200 sec⁻¹ with the step of 40. The measurement at each fraction and temperature was carried out until the relative error of three successive measurements became less than 1%.

RESULTS AND DISCUSSION

Viscosity Properties of Urethane Acrylate Cationomers in Aqueous Media

Figure 3 shows the results of shear stress versus shear rate for MUAC

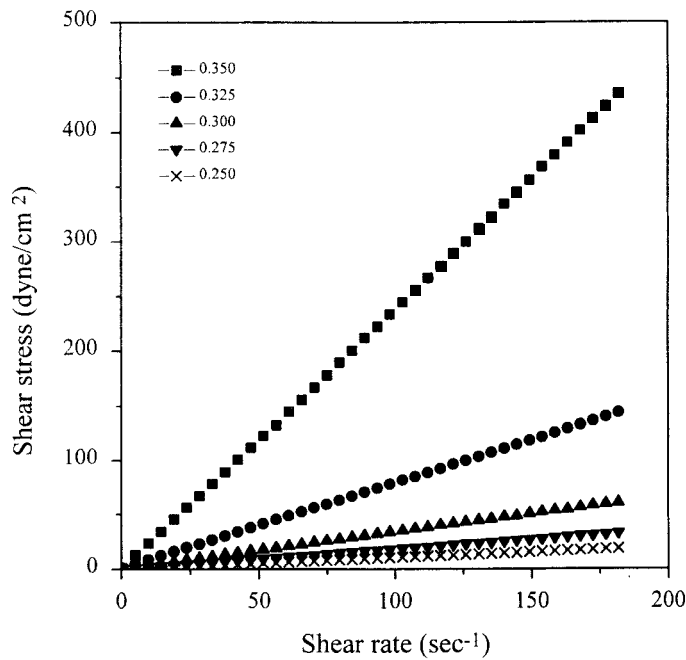


Figure 3. Shear stress versus shear rate for MUAC in solutions of different fractions at the temperature of 30°C.

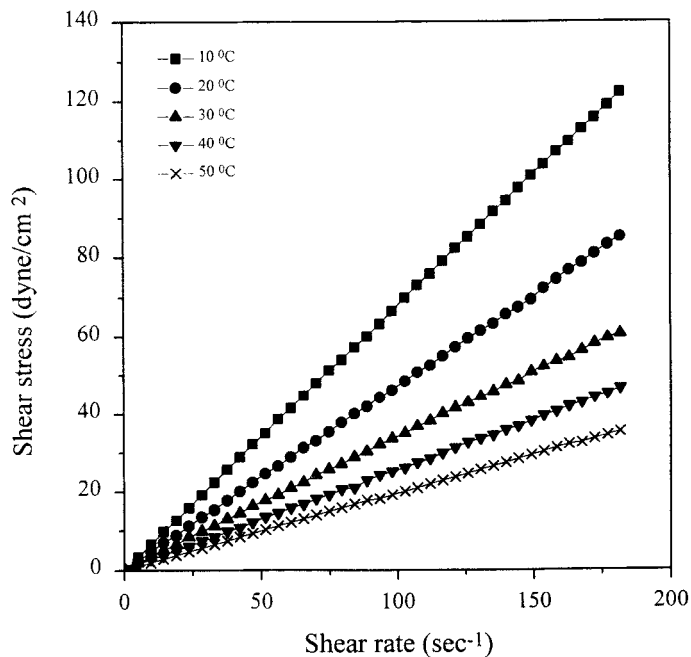


Figure 4. Shear stress versus shear rate for MUAC solutions of different temperatures at the fraction of 0.30.

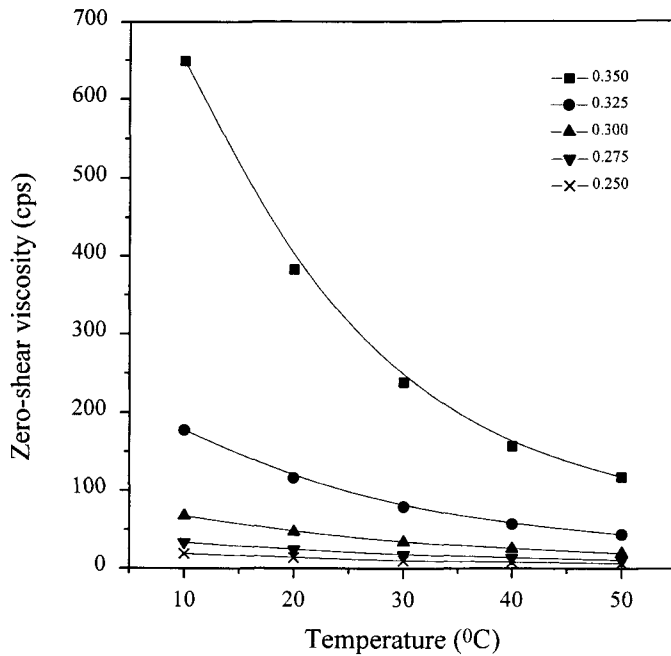


Figure 5. The viscosity of MUAC solution of different fractions as a function of temperature.

solutions with the fraction at 30°C. All curves on Figure 3 were linear, indicating that the shear stress of MUAC solution was shear rate independent at the given resin fractions. Figure 4 shows shear stress versus shear rate for MUAC solutions with the temperature at the fraction of 0.30. Similarly, all curves of Figure 4 were linear. It also represented that the shear stress was shear rate independent within the given temperature ranges.

The viscosities of MUAC solutions of different fractions are shown as a function of temperature in Figure 5. The viscosity of MUAC solution and temperature were correlated using the Arrhenius equation:

$$\eta_0 = \eta_\infty e^{E/RT} \tag{1}$$

$$\ln \eta_0 = \ln \eta_\infty + E/RT \tag{2}$$

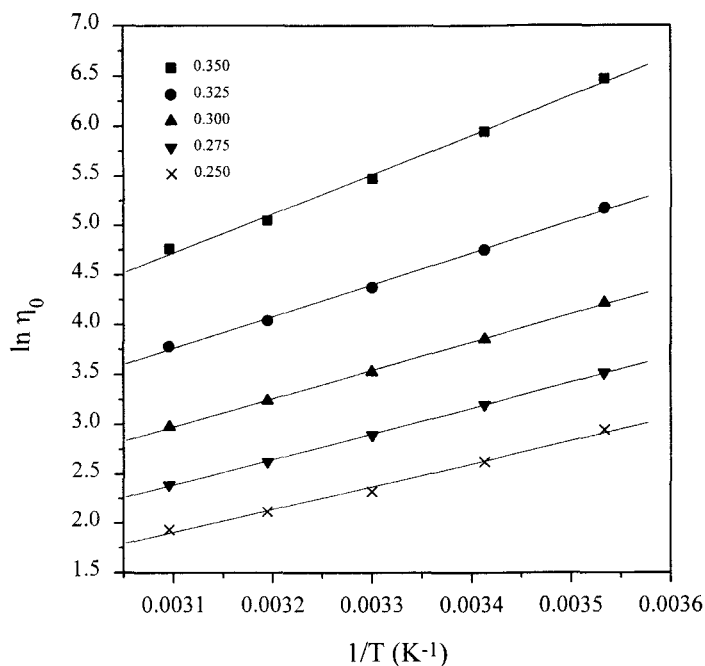


Figure 6. Logarithmic viscosity versus reciprocal temperature.

where, η_0 is the solution viscosity, infinite viscosity, E the activation energy of the solution, $R = 8.314 \text{ J/molK}$, and T temperature in K. The results of Figure 5 were rearranged using Equation 2 and shown in Figure 6. The slope of the line represents the activation energy and the Y-axis intercept shows the logarithmic infinite viscosity, $\ln\eta_\infty$. The $\ln\eta_\infty$ and the activation energy for MUAC solution are shown against the fraction of MUAC in Figure 7. From Figure 7, we could obtain the result of increasing activation energy and decreasing $\ln\eta_\infty$ with the fraction. This reflected that the molecular interaction increased gradually as the fraction increased. As such molecular interactions, MUAC can have Coulombic interaction by cationic groups, hydrophobic interaction by polyethers, and hydrogen bond of urethane linkages and polyethers.

In Figure 7, it was of interest to note that the activation energy and $\ln\eta_\infty$ deviated from linear relationship above the fraction of 0.325. This result was interpreted in terms of molecular interactions. Above the fraction of 0.325, the MUAC chains interact intermolecularly radially, causing a sharp viscosity increase [11]. Regarding the intermolecular interaction, there was a marked difference in the

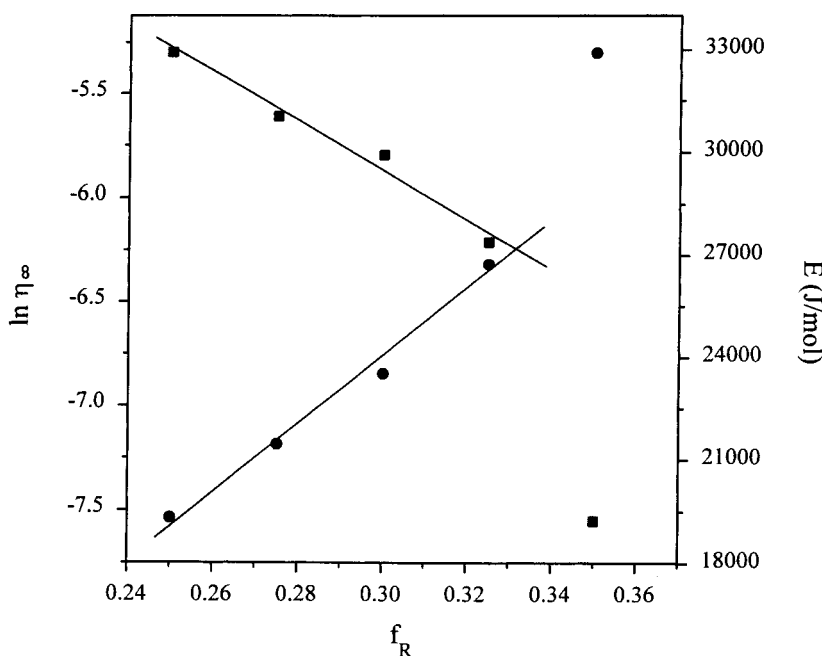


Figure 7. MUAC fraction versus the logarithmic viscosity and the activation energy (J/mol). - ● - is the activation energy of MUAC solution and - ■ - is η_∞ .

viscosity behavior of MUAC from those of polyelectrolytes and ionomers [12-16]; the intermolecular interactions of MUAC chains occurred at much higher fraction region. This result seemed to be attributed to the lower molecular weight of MUAC, compared to polyelectrolytes and ionomers.

Theoretical Approach to Obtain the Rheological Equation of State

As shown in Figure 7, for MUAC solutions, both \ln and activation energy showed linear correlation with the fraction of MUAC below the fraction of 0.325. This linear correlation proposed $\ln \eta_\infty$ and activation energy could be empirically expressed as a function of composition. Therefore, below the fraction of 0.325, the following relationship was possible:

$$E = E_1 + E_2 f_R \tag{3}$$

$$\ln \eta_\infty = a_1 + a_2 f_R \tag{4}$$

where, E_1 is the extrapolated activation energy, E_2 the slope of Figure 7, a_1 the extrapolated infinite viscosity, and a_2 the slope of Figure 7. Substituting Equations 3 and 4 into Equation 1, one could obtain:

$$\begin{aligned}\eta_0 &= e^{(a_1 + a_2 f_R)} e^{(E_1 + E_2 f_R)/RT} \\ &= e^{(a_1 + E_1/RT)} e^{(a_2 + E_2/RT) f_R}\end{aligned}\quad (5)$$

Therefore, the following functional relationship could be suggested:

$$\eta_0 = f(f_R, 1/T) \quad (6)$$

Equation 6 means that the viscosity of urethane acrylate cationomer solution has function relationship with the fraction and reciprocal temperature.

By taking mutual log of both sides of Equation 5, the following rheological equation of state could be obtained:

$$\ln \eta_0 = a_1 + E_1/RT + (a_2 + E_2/RT) f_R \quad (7)$$

The derivative $[\ln \eta_0 / \partial(1/T)]_{f_R}$ at a fixed fraction has the form,

$$[\partial \ln \eta_0 / \partial(1/T)]_{f_R} = (E_1 + E_2 f_R)/R \quad (8)$$

The derivative $[\partial \ln \eta_0 / \partial f_R]_{1/T}$ at a fixed temperature has the form,

$$[\partial \ln \eta_0 / \partial f_R]_{1/T} = a_2 + E_2/RT \quad (9)$$

Thermodynamic criterion for Equation 7 shows

$$\partial^2 \ln \eta_0 / \partial(1/T) \partial f_R = \partial^2 \ln \eta_0 / \partial \eta f_R \partial(1/T) = E_2/R \quad (10)$$

To verify Equation 7, the thermodynamic equation of state, the derivatives, J and D, for MUAC solution must be determined experimentally.

$$J = \partial^2 \ln \eta_0 / \partial(1/T) \partial f_R \quad (11)$$

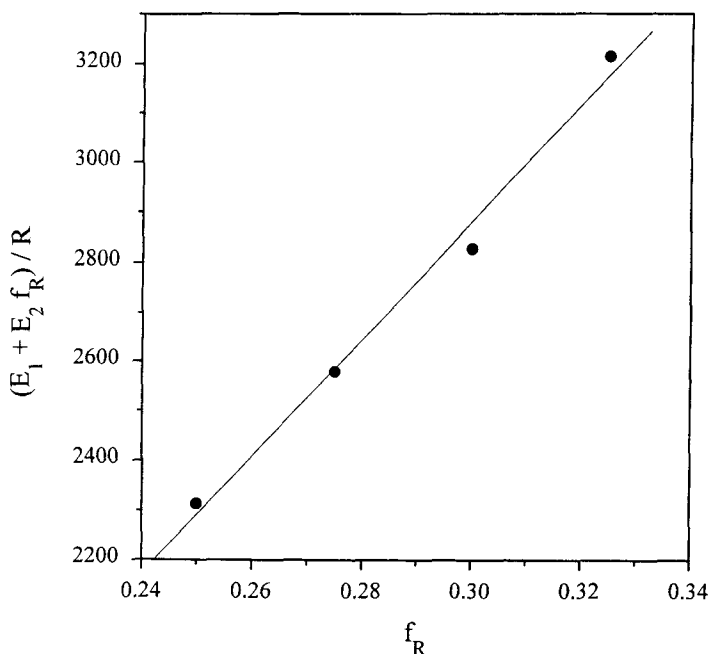


Figure 8. MUAC fraction versus $(E_1 + E_2 f_R) / R$.

$$D = \partial^2 \ln_0 / \partial f_R \partial (1/T) \tag{12}$$

Viscosity Prediction through Obtained Rheological Equation of State

Equation 7 proposed as a thermodynamic equation of state must satisfy thermodynamic criterion. Therefore, it must be verified that Equations 12 and 13, J and D, have the same values. The slopes in Figure 6 represent $(E_1 + E_2 f_R) / R$. The values of $(E_1 + E_2 f_R) / R$ at different f_R were determined and plotted against f_R in Figure 8. The slope in Figure 8 corresponded to J of Equation 11. J obtained had the value of 11818.600.

The logarithmic viscosity versus MUAC fraction is shown for different temperatures in Figure 9. The logarithmic viscosity was regressed linearly. From the slope in Figure 9, the values of $a_2 + E_2 / RT$ were determined and plotted against reciprocal temperature in Figure 10. The slope in Figure 10 corresponded to D of Equation 12. D obtained had the value of 11689.980.

A negligible difference between J and D could be obtained, indicating Equation 7 satisfied the thermodynamic criterion. This result suggested that MUAC

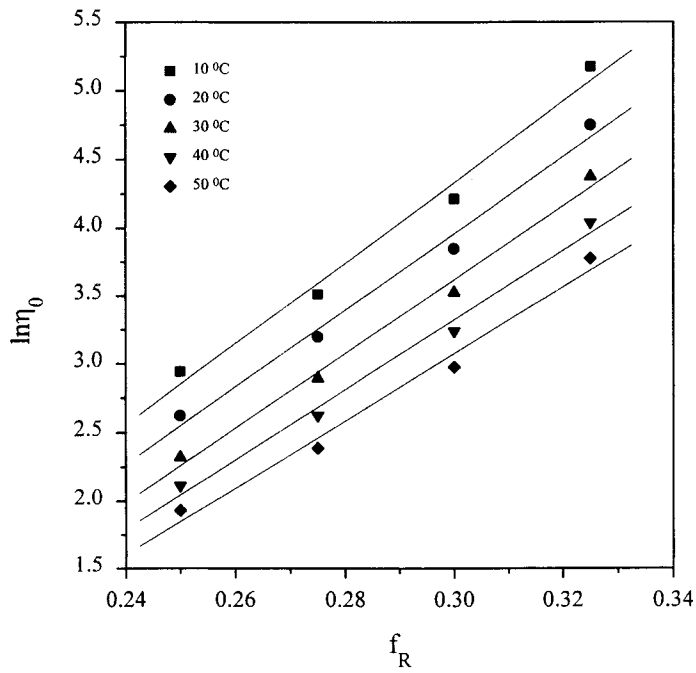


Figure 9. Logarithmic viscosity versus MUAC fraction.

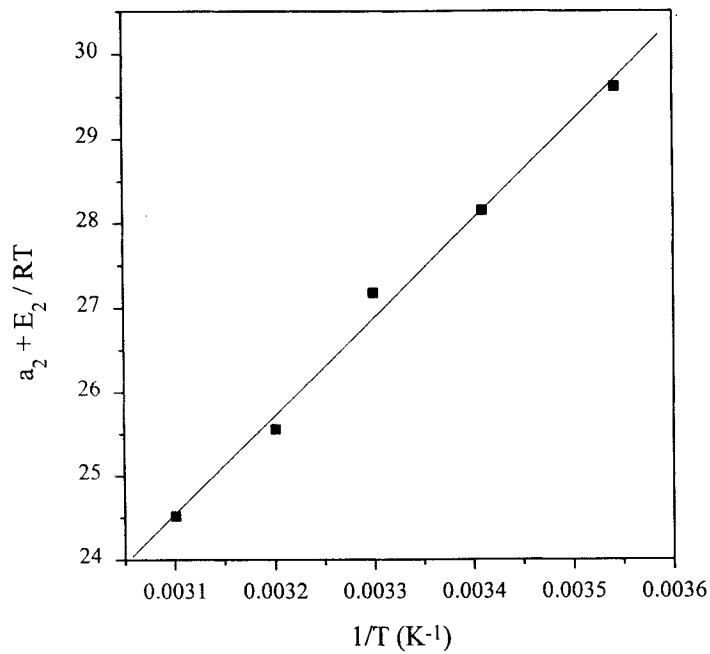


Figure 10. $1/T$ versus $a_2 + E_2/RT$.

TABLE 2. Comparison of $\ln \eta_o$ measured with $\ln \eta_o$ Calculated

f_R	$1/T$ (K^{-1})	\ln_o (experimental)	\ln_o (theoretical)	error %
0.25	0.0035	2.944	2.843	3.55
0	3	2.625	2.567	3
0.25	0.0034	2.322	2.315	2.25
0	1	2.116	2.063	9
0.25	0.0033	1.932	1.856	0.30
0	0			2
0.25	0.0031			2.56
0	9			9
0.25	0.0031			4.09
0	0			5
0.27	0.0035	3.512	3.583	1.98
5	3	3.198	3.272	2
0.27	0.0034	2.896	2.987	2.26
5	1	2.625	2.703	2
0.27	0.0033	2.389	2.470	3.04
5	0			7
0.27	0.0031			2.88
5	9			6
0.27	0.0031			3.27
5	0			9
0.30	0.0035	4.215	4.322	2.47
0	3	3.850	3.977	6
0.30	0.0034	3.526	3.660	3.19
0	1	3.239	3.343	3
0.30	0.0033	2.976	3.083	3.66
0	0			1
0.30	0.0031			3.11
0	9			1
0.30	0.0031			3.47
0	0			1
0.32	0.0035	5.178	5.062	2.29
5	3	4.754	4.681	2
0.32	0.0034	4.377	4.332	1.55
5	1	4.041	3.983	9
0.32	0.0033	3.780	3.697	1.03
5	0			9
0.32	0.0031			1.45
5	9			6
0.32	0.0031			2.24
5	0			5

solution followed well the thermodynamic equation of state, and the rheological equation of state, (Equation 7), was state functions of fraction and reciprocal temperature.

By taking an average value of J and D, 11754.290 could be obtained. E_1/R and a_2 obtained were -644.956 and -11.899, respectively. Also, the value of a_1 in Equation 7 could be obtained using the value of E_1/R and a_2 , and a_1 showed the value of -2.279. From the constants of E_1/R , a_2 , and a_1 , the Equation 7 could be expressed again as following :

$$\ln \eta_0 = -2.279 - 644.956 / T + (-11.899 + 11754.290 / T) f_R \quad (13)$$

In Table 2, the logarithmic viscosities measured were compared to logarithmic viscosities calculated from Equation 13 as functions of MUAC fraction and reciprocal temperature. The experimental error was within the maximum of 4.095%. The viscosities calculated from rheological equation of state of Equation 13 showed good correspondence to the viscosities measured. From this result, the rheological equation of state could be used predicting the viscosities of MUAC solution.

CONCLUSION

The logarithmic viscosities of MDEA-incorporated urethane acrylate cationomer (MUAC) synthesized as a water-soluble urethane acrylate followed the Arrhenius equation well. In this study, the correlation between viscosity and resin fraction was considered, and an interesting result that the logarithmic infinite viscosity and activation energy had the linear relationship with the fraction of MUAC below the fraction of 0.325 could be obtained. Above the fraction of 0.325, the deviation from the linear relationship was observed. This result was interpreted in terms of the occurrence of intermolecular interactions among MUAC chains. By using the linear relationship of infinite viscosity and activation energy with the fraction of MUAC, rheological equation of state could be proposed. The rheological equation of state agreed well with the experimental data within the error % of about 4.

ACKNOWLEDGEMENT

The author wishes to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998. J. W. Kim is grateful to the Graduate

School of Advanced Materials and Chemical Engineering at the Hanyang University for a fellowship.

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Received June 25, 1997

Final revision received March 1, 1998