

Aqueous Dispersion of Polyurethanes from H₁₂MDI, PTAd/PPG, and DMPA: Particle Size of Dispersion and Physical Properties of Emulsion Cast Films

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SYNOPSIS

Aqueous dispersions of ionic/nonionic polyurethane (PU) were prepared from hydrogenated diphenylmethane diisocyanate (H₁₂MDI), poly(tetramethylene adipate) glycol (PTAd), polypropylene glycol (PPG), monofunctional ethylene-propylene oxide ether, and dimethylol propionic acid (DMPA). The effects of DMPA, PTAd/PPG ratio, and the average molecular weight of PPG on the state of dispersion, mechanical, and viscoelastic properties of the emulsion cast films were determined using Autosizer, Instron, and Rheovibron.

INTRODUCTION

Polyurethane (PU) ionomer can be defined as a PU consisting of PU backbone with a minority of pendant acid groups that are neutralized to form salts.¹ The presence and amount of ionic groups have a significant effect on many of their physical properties due mainly to the existence of Coulombic forces between the ionic centers.² The ionomers are hydrophilic in nature³ and, hence, dispersible in aqueous medium. This is a most significant feature of ionomer over solvent type from an environmental point of view. Aqueous dispersion of PU can also be obtained from nonionic hydrophilic polyols, predominantly from polyethylene oxide.⁴ However, aqueous PU dispersion from nonionic polyether-type polyol is unstable at elevated temperatures above 60°C,⁵ and film formed from this is inferior in strength to the ionomer. Recently, attempts have been made to combine both ionic and nonionic segments in one PU, and a synergistic effect in terms of dispersion stability has also been reported.⁶⁻⁸

In the preparation of aqueous PU dispersion, control of particle size is also of significant importance with regard to the specific application of PU

dispersion.¹ For example, rapid drying is achieved in coating with relatively large particles.

This paper describes the preparations of PU ionomers from PTAd, PPG, and DMPA as anionic centers. Nonionic hydrophilic segments, viz. monofunctional ethylene-propylene oxide ether (EOE), were also incorporated. Effects of DMPA, PTAd/PPG ratio, and molecular weight of PPG on the state of dispersion and physical properties of emulsion cast films were examined.

EXPERIMENTAL

Materials

PTAd ($M_n = 1016$, Dongsung Chemicals), and PPG ($M_n = 400, 1000$, Korea Polyols) were dried at 0.1 mmHg, 80°C for 3 h before use. H₁₂MDI (Mobay) was distilled under high vacuum ($\sim 10^{-3}$ mmHg) before use. EOE ($M_n = 1930$) was synthesized from 1-butanol, ethylene oxide (EO), and propylene oxide (PO) with molar ratio of EO to PO of 87 : 13. Extra-pure grades of triethylamine (TEA) and triethylenetetramine (TETA) were dried over 3 Å molecular sieve for 3 days. Other extra-pure grades of reagent, DMPA, *N*-methyl-2-pyrrolidinone (NMP), and dibutyltin dilaurate (DBT, T-12) were used without further purification.

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Procedure

Urethane-forming reactions were carried out in a 500 mL round-bottom, four-necked separable flask, equipped with a mechanical stirrer, nitrogen inlet, condenser, and pipet outlet. Reactions were carried out in a constant temperature oil bath with $\pm 0.5^\circ\text{C}$ precision. Formulations are given in Table I, and the reaction scheme is shown in Figure 1. PTAd, PPG, EOE, and DMPA dissolved in NMP were charged to the reactor and heated to 80°C with agitation to homogenize the mixture. While keeping the temperature at 80°C , the reaction proceeded over approximately 4 h, and the progress of reaction was followed by determining the NCO values using standard dibutylamine back titration.⁹ Upon obtaining the theoretical NCO value to complete NCO terminated prepolymer, the mixture was cooled to 60°C and the carboxylic groups were neutralized with TEA. Aqueous dispersion was obtained by adding water dropwise to the mixture. A tubing

pump was employed to control the flow rate. Chain extension was carried out with TETA/water for a period of 3 h. NMP was added in several steps to lower the solution viscosity, and the total amount was adjusted around 10% of emulsion.

Tests

Particle-size analysis was done using light-scattering equipment (Autosizer, Melvern IIC), and mechanical and viscoelastic properties of the emulsion cast films were determined using an Instron and a Rheovibron (Tokyo Baldwin DDV-II). Tensile tests were made at room temperature following ASTM D-412 with type C specimen. At least three runs were done to report the average value. Rheovibron tests were performed from -150 to 80°C , at 11 Hz. Films were prepared by casting the emulsion on a Teflon plate, followed by drying at 40°C for 24 h. Remaining moisture was dried off at 30°C , 20 mmHg, for the next 24 h.

Table I Feed Composition (in grams)

(A) Variation of DMPA Content										
Run #	DMPA (wt %)	EOE	PTAd	PPG	H ₁₂ MDI	DMPA	TEA	TETA	Water	NMP
HD-1	3.18	0.90	14.55	9.02	16.92	1.4315	1.07	1.0797	70.71	12.46
HD-2	3.49	0.90	14.30	8.87	17.05	1.5714	1.19	1.0881	70.71	12.46
HD-3	3.82	0.90	14.03	8.70	17.23	1.7167	1.29	1.0991	70.71	12.46
HD-4	4.13	0.90	13.77	8.54	17.37	1.8621	1.40	1.1085	70.71	12.46
HD-5	4.43	0.90	13.54	8.40	17.49	1.9939	1.50	1.1163	70.71	12.46
(B) Variation of PPG Content										
Run #	PPG (wt %)	PTAd	PPG	H ₁₂ MDI	DMPA	TEA	TETA	NMP	Water	
HP-1	0.0	29.38	0.00	14.73	1.6793	1.27	0.9402	14	75	
HP-2	3.9	26.38	1.87	15.62	1.7804	1.34	0.9968	14	75	
HP-3	8.3	23.00	3.99	16.62	1.8946	1.52	1.0607	14	75	
HP-4	13.3	19.16	6.40	17.76	2.0243	1.52	1.1333	14	75	
HP-5	19.1	14.76	9.15	19.06	2.1727	1.64	1.2164	14	75	
(C) Variation of PPG M _n										
Run #	PPG (M _n)	EOE	PTAd	PPG	H ₁₂ MDI	DMPA	TEA	TETA	Water	NMP
HP-5	400	0	14.76	9.15	19.06	2.1727	1.64	1.2164	75.43	13.29
HW-1	600	0	13.47	12.53	17.40	1.9836	1.49	1.1105	75.43	13.29
HW-2	800	0	12.39	15.37	16.01	1.8248	1.38	1.0216	75.43	13.29
HW-3	1000	0	11.47	17.79	14.82	1.6896	1.27	0.9459	75.43	13.29

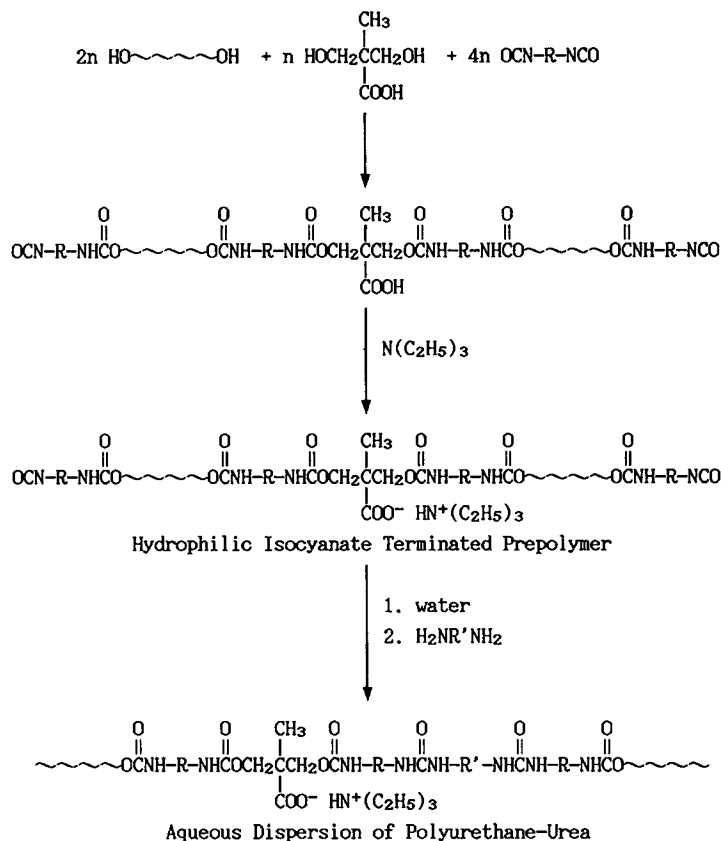


Figure 1 Reaction scheme.

RESULTS AND DISCUSSION

Effect of DMPA

In this series of experiments, contents of PPG ($M_n = 400$, 19.1% based on total solids) and EOE (2%) were kept constant, and the DMPA content was varied 3.18–4.43 wt %.

Particle size and its distribution (Fig. 2) are almost independent of DMPA content. In aqueous PU dispersion, particle size decreases with increasing hydrophilicity of PU,¹⁰ and it was observed that the particle size is reduced from 0.7 to 0.1 μm when bisphenol A ethylene-propylene oxide ether glycol was used instead of PPG, at the same conditions (unpublished results). The independence of particle size on DMPA content is probably due to the hydrophilic nature of PPG, that is, added DMPAs do not change the total hydrophilicity of PU. Moduli (Fig. 3), tensile strength, and elongation at break (Fig. 4) for the emulsion cast films show strong dependence on DMPA content. The increase of tensile properties with DMPA comes directly from the increased number of urethane linkages and interchain interactions of PU ionomers via Coulombic forces.¹¹ With

the increase of DMPA content, the amount of polyols incorporated in the PU structure is reduced in stoichiometric fashion. This produces more urethane linkages to form hard domains together with isocyanate segments. The Coulombic forces generated between the ionic centers are the source of improved mechanical properties of ionomers over conventional

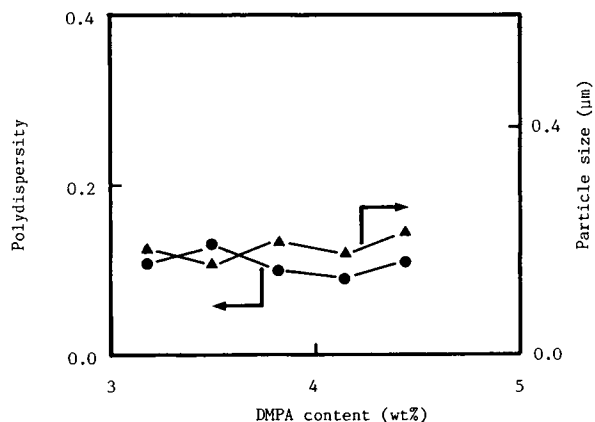


Figure 2 Average particle size and polydispersity as a function of DMPA content [Table I(A)].

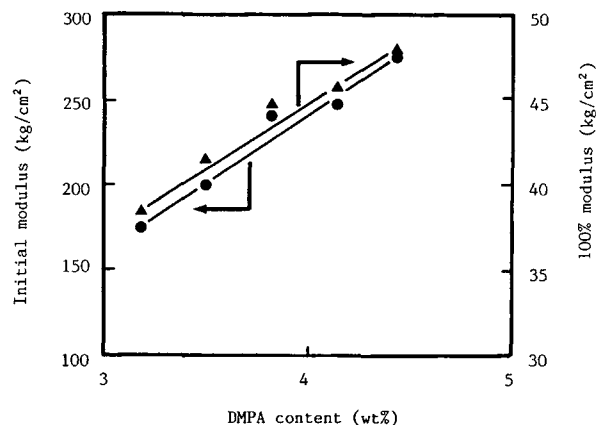


Figure 3 Effect of DMPA on initial modulus of PU ionomer [Table I(A)].

solvent-type PU.² With increased stiffness and strength, PU ionomers lose their ductility as DMPA content increases (Fig. 4).

Dynamic responses of emulsion cast films in the temperature range -100 to 80°C are shown in Figure 5 and 6. Storage modulus (E') is directly related to load-bearing capabilities,¹² and this increases with DMPA content, a result consistent with the mechanical property dependence on DMPA content. It is noted that the loss peak (Fig. 6) moves toward higher temperature as the DMPA content increases, indicative of increased stiffness of the chains.

Effect of PPG Content

The effects of PPG ($M_n = 400$) contents on particle size and physical properties of emulsion cast films were examined at fixed DMPA content (4.43 wt %). The content of PPG varied from 0 to 19.1 wt %

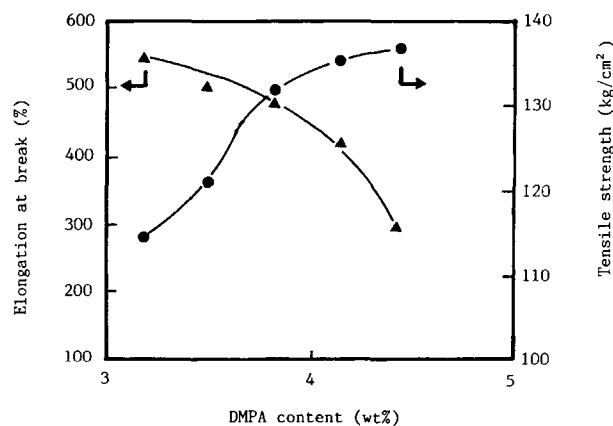


Figure 4 Effect of DMPA on tensile strength and elongation at break of PU ionomer [Table I(A)].

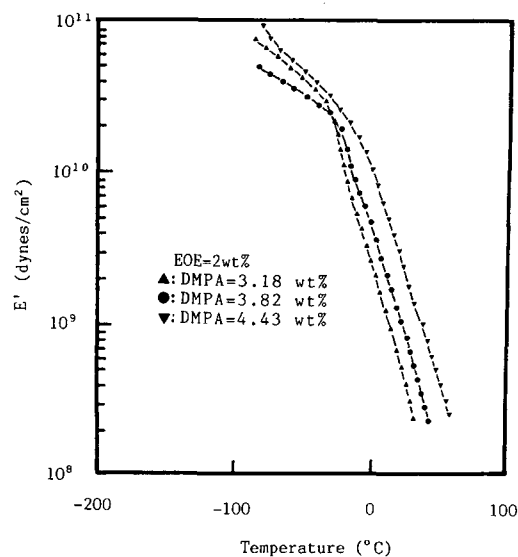


Figure 5 Effect of DMPA on storage moduli of PU ionomer [Table I(A)].

based on total solid. Particle size increases slowly at low and rapidly at high PPG contents (Fig. 7). The increase of particle size with PPG is most likely due to the temperature sensitivity of polyether polyol in water. Polyether loses its hydrophilicity as temperature goes up, and at about 65°C its hydrophilicity is completely lost.¹ At the emulsification temperature (60°C), only small amounts of PPG chains should be soluble in water. Excess amount over the solubility limit should reduce the total hydrophilicity of the PU, leading to increase of particle size.

Initial modulus (Fig. 8) and tensile strength (Fig.

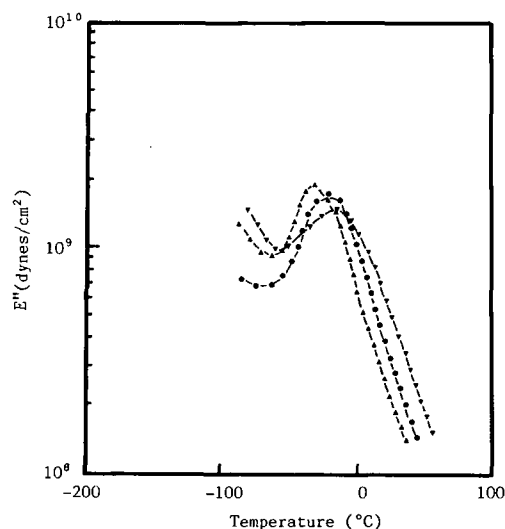


Figure 6 Effect of DMPA on loss moduli of PU ionomer [Table I(A)].

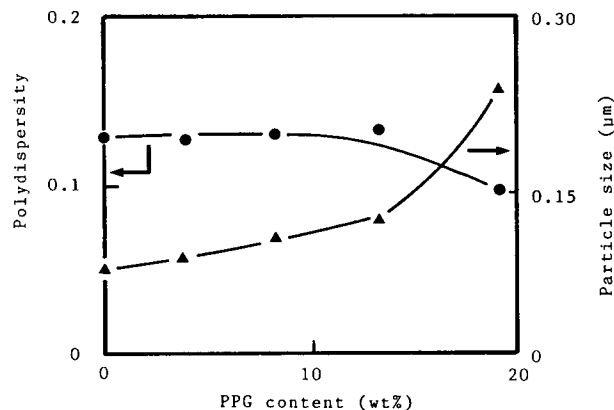


Figure 7 Average particle size and polydispersity as a function of PPG content [Table I(B)].

9) increase slowly at low and rapidly at high PPG contents. This should come from the competitive effects of increased number of urethane linkages and decreased interchain interactions.¹¹ Molecular weight of PPG used in this series of experiments was about 400, and that of PTAd, 1016. With low M_n polyol, more urethane linkages are formed upon reaction with isocyanates.¹³ On the other hand, interchain interactions of the ether-type polyol (PPG) are weaker than those of the ester-type polyol (PTAd). In addition, methyl branches in PPG should, in part, contribute to the mechanical properties in amorphous polymers. With increased modulus and strength, elongation at break decreases as the PPG content increases (Fig. 9).

Effect of PPG Molecular Weight

In this series of experiments, DMPA content was fixed at 4.43 wt %, and the M_n of PPG varied, 400–

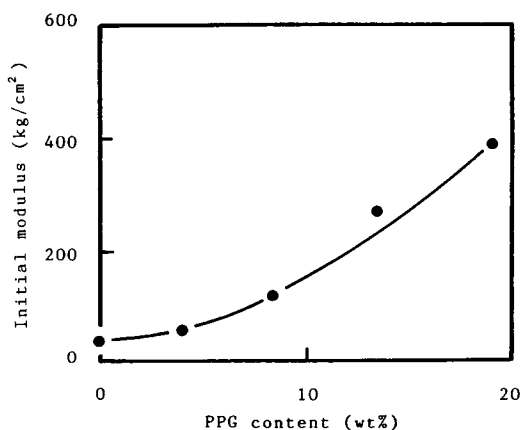


Figure 8 Effect of PPG on initial modulus of PU ionomer [Table I(B)].

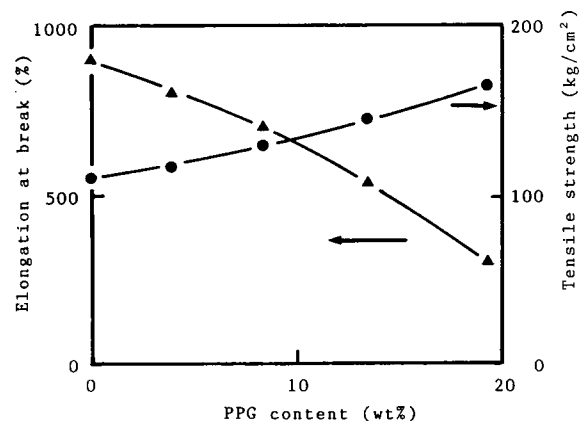


Figure 9 Effect of PPG on tensile strength and elongation at break of PU ionomer [Table I(B)].

1000 g/mol. Number-average particle size decreases (Fig. 10) as the M_n increases. Polyols in PU form soft segments, and as the M_n of polyols increases, PU chains lose their rigidity and strength, not solely by their fractional increase in weight but also from the reduced number of urethane linkages, which with isocyanate segments form hard domains.¹⁴ Therefore, a decrease in modulus (Fig. 11) and tensile strength (Fig. 12) and an increase in ductility (Fig. 12) are expected.

The reduction of elastic modulus (E') with the increase of M_n in dynamic experiments is shown in Figure 13. As the M_n increases, the loss peak (Fig. 14) also moves toward low temperature and the peak area is reduced. Since the loss peak corresponds to the α -transition of hard domains,¹⁵ the reduced area can be interpreted in terms of reduced hard domain interactions.^{16,17} With reduced numbers of urethane linkages, reduced interactions are expected.

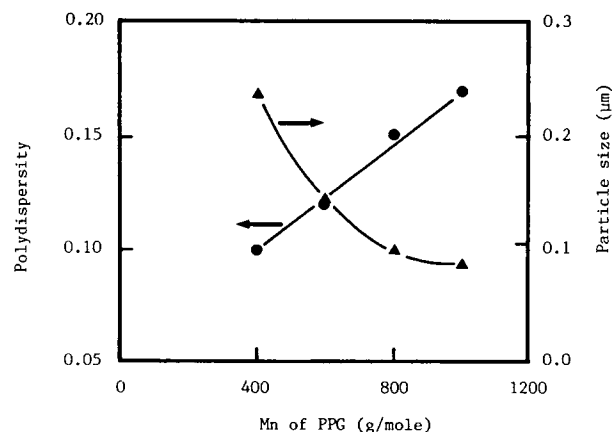


Figure 10 Average particle size and polydispersity as a function of M_n of PPG [Table I(C)].

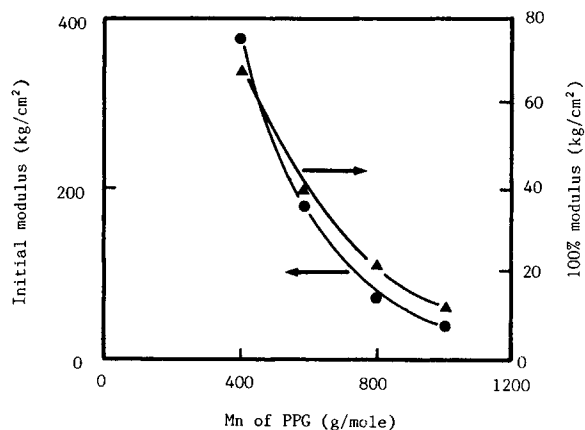


Figure 11 Effect of M_n of PPG on initial modulus of PU ionomer [Table I(C)].

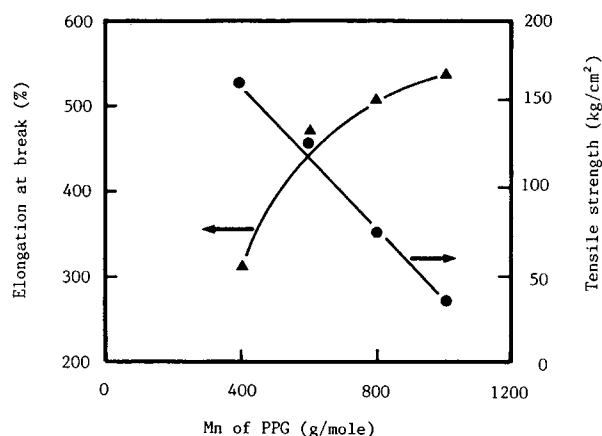


Figure 12 Effect of M_n of PPG on tensile strength and elongation at break of PU ionomer [Table I(C)].

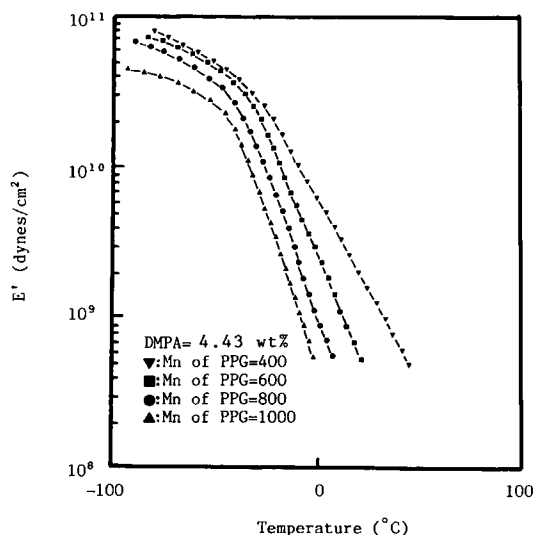


Figure 13 Effect of M_n of PPG on storage moduli of PU ionomer [Table I(C)].

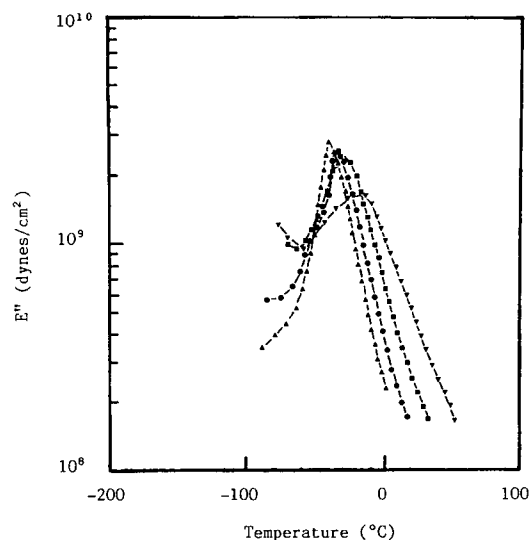


Figure 14 Effect of M_n of PPG on loss moduli of PU ionomer [Table I(C)].

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