

# Molecular Parameters and Their Relation to the Adhesive Performance of Acrylic Pressure-Sensitive Adhesives

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**ABSTRACT:** Model acrylic pressure-sensitive adhesives (PSAs) based on poly(2-ethyl-hexyl acrylate-stat-acrylic acid) and poly(*n*-butyl acrylate-stat-acrylic acid) at 97.5/2.5 wt % were synthesized using semicontinuous emulsion and solution polymerizations. Microgels formed in the lattices retained their discrete network morphology in the film. In contrast, acrylic solution was essentially gel free and crosslinking in the film was provided by the reaction of acrylic acid and post added Al Acetyl Acetonate after solvent evaporation, which led to continuous network morphology. The difference in film network morphology caused significantly lower shear holding power for the film from emulsion PSA compared with that of solvent-borne film. Unlike shear holding power, loop tack and peel of acrylic PSAs were mainly controlled by the same sol/gel molecular parameters, regardless of emulsion or solution PSAs. The important molecular parameters are sol-to-gel ratio, entanglement molecular weight, weight average molecular weight, and to a lesser extent, glass transition temperature. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2230–2244, 2001

**Key words:** PSAs; acrylic; synthesis; emulsion; network

## INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic-elastomeric materials that can adhere strongly to solid surfaces upon application of light contact pressure and short contact time. Commercial use of PSA covers a broad range of label, tape, medical, and cosmetic products.

Among different base polymers used in making PSAs, high alkyl acrylates, such as poly(*n*-butyl acrylate), poly(2 ethyl-hexyl acrylate), and poly(iso-octyl acrylate), have enjoyed the fastest growth in commercial applications.<sup>1</sup> Their popu-

larity is mainly attributable to optical clarity, oxidative and ultraviolet resistance, migration resistance, low toxicity, and low cost. Acrylic PSA polymers are coated onto tape or label in the forms of either hot melt, solvent borne, or water borne. Because acrylic PSAs comprise polymers having high entanglement molecular weight ( $M_e \geq 15,000$  g/mol), low glass transition temperature ( $T_g$ ) ( $T_g \leq -20^\circ\text{C}$ ), and medium to low molecular weight ( $M_w \leq 400,000$  g/mol), some types of crosslinking must be provided to yield high shear holding power. In hot melt acrylic PSA, crosslinking is provided by ultraviolet radiation.<sup>2</sup> In solvent-borne acrylic, crosslinking is provided by the reaction of acrylic acid copolymer, with either  $\text{AlO}_3$  or  $\text{TiO}_4$  upon the evaporation of solvent.<sup>3</sup> In water-borne acrylic, intraparticle crosslinking oc-

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curs as part of the chain transfer to polymer during emulsion polymerization,<sup>4</sup> and microgels are formed inside the latex particles.

Despite the rapid pace in commercialization of PSAs, fundamental understanding of how PSA works has taken small evolutionary steps. The first phenomenological postulate on PSA characteristics was provided by Dahlquist.<sup>5</sup> PSA materials were those that had 1-s creep compliance  $>10^{-6}\text{cm}^2/\text{dyne}$ . In the early 1980s, Aubrey and Sheriff<sup>6</sup> discussed the relationship between various failure modes in peel test such as stick-slip, glassy fracture, and fibrillation (viscous flow or rubbery plateau) to frequency sweep master curve from dynamic mechanical analysis (DMA). Although Dahlquist's postulate addresses the need of rapid viscous flow to achieve intimate contact between the substrate and PSA, providing that the PSA is able to wet the substrate, it does not consider the viscoelastic energy dissipation during peeling of a PSA tape. In the 1990s, Chang<sup>7,8</sup> developed the direct relationship between peel energy and the ratio between shear-loss modulus ( $G''$ ) measured at 437 rad/s to storage modulus ( $G'$ ) measured at 1 rad/s using DMA. The first molecular approach in explaining PSA material behavior during the debonding process was given by Zosel.<sup>9</sup> To impart high debonding energy, PSA had to yield fibrils of 10–100  $\mu\text{m}$  in diameter and 500–1000  $\mu\text{m}$  in length during debonding or peeling. Only those polymers with entanglement molecular weight  $>10,000$  g/mol were able to show fibrillation during debonding.

Because acrylic PSAs contain both gel and sol fractions, understanding the molecular parameters and their relation to PSA performance such as tack, peel, and shear holding power are critical. In the previous study,<sup>10</sup> it was found that the low shear holding power in tackified acrylic emulsion was caused by the lack of entanglement between the molecules connecting the microgels. Furthermore, rapid diffusion of the sol fraction polymer was implicated to contribute to the mixing of the polymer and high  $T_g$  tackifier which negated the effect of the drying temperature. Therefore, the performance of tackified acrylic emulsion is strongly dependent on the molecular characteristics of the neat acrylic emulsion as long as the tackifier is thermodynamically miscible with the polymer.

This research focuses on the relationship among various molecular parameters in acrylic emulsion PSA to adhesive performance. Molecular parameters of interest are molecular weight, gel content,

entanglement molecular weight ( $M_e$ ), molecular weight between crosslink points ( $M_c$ ), network morphology, and  $T_g$ . Adhesive performance measured were looptack, peel, and shear holding power. Model acrylic emulsion PSAs based on poly(2 ethylhexyl acrylate-stat-acrylic acid) [P(2EHA-stat-AA)] 97.5/2.5 and poly(*n*-butyl acrylate-stat-acrylic acid) [P(BA-stat-AA)] 97.5/2.5 by weight were synthesized using semicontinuous emulsion polymerization. As a comparison, acrylic solution PSAs of the same monomeric composition were synthesized using semicontinuous solution polymerization. Monodisperse poly(*n*-butyl acrylate) and poly(2 ethylhexyl-acrylate) made by anionic polymerization<sup>11</sup> were characterized using DMA to establish the correct  $M_e$  and  $T_g$  values that are not affected by polydispersity. Using the correct  $M_e$  values,  $M_e$  for polydisperse polymers could then be estimated using the plasticizer model.<sup>12</sup>

## EXPERIMENTAL

### Materials

The monodisperse poly(2-ethylhexyl acrylate) [P(2EHA)] and poly(*n*-butyl acrylate) [P(*n*BA)] were purchased from Polymer Source, Inc. The number average molecular weights ( $M_n$ ) of P(BA) and P(2EHA) are 226,000 and 214,000 g/mol, respectively.

The 2EHA, *n*BA, and AA monomers were all commercial grades available from Elf-Atochem. 2-Ethylhexyl methacrylate (2-EHMA) was obtained from Rohm America.

The initiator potassium persulfate (KPS) was obtained from Aldrich. Water soluble AIBN initiator, Wako V-50® [2,2'-Azobis (2-amidino propane) dihydrochloride] was obtained from Wako Chemicals. Oil soluble AIBN, Vazo® 67, was obtained from DuPont.

The surfactant used was nonyl-phenol ethoxylate sulfate having 4 ethylene-oxide unit (Polystep® B-27) from Stepan Chemical Co. Its activity in  $\text{H}_2\text{O}$  is 30% by weight.

The aqueous tackifier dispersion was based on glycerol ester abietic acid ( $M_w = 940$ , PDI = 1.1, DMA  $T_g = 64^\circ\text{C}$ ), Snowtack® 920, from AKZO NOBEL. The mean particle diameter for the tackifier dispersion was  $514 \pm 202$  nm and the solid content was 58%. The dried version of this tackifier (including the surfactant) was dissolved in toluene to be used for tackification of solvent-borne acrylic PSAs.

Chain transfer agent, *n*-Dodecyl Mercaptan (*n*-DDM) was obtained from Aldrich.  $\text{NH}_4\text{OH}$  (25% concentration by weight in  $\text{H}_2\text{O}$ ) was obtained from Textile Chemicals. Kathon LX (Biocide) was obtained from Rohm & Haas.

### Preparation of Acrylic PSA Using Semicontinuous Emulsion Polymerization

#### Preparation of Monomer Emulsion

One hundred thirty-three grams of deionized (DI) water and 67 g of Polystep B27 surfactant (30% active) were mixed using a magnetic stirrer. Separately, 434 g of 2EHA (or BA) and 11 g of AA were mixed. The water-surfactant mixture was placed under high shear agitator at 150 rpm. The monomer mixture was slowly added into the water-surfactant mixture by pouring into the agitator blades over a 20-min period. The resulting monomer emulsion was milky in appearance.

#### Preparation of Initiator Solution

The initiator solution was made by adding 1.14 g of KPS into 40.4 g of DI water and stirred in using a magnetic bar. The amount of KPS is equivalent to 0.256 parts per hundred part of monomer (pphm).

#### Polymerization Procedure

Two hundred eighteen grams of DI water in a 1-L glass kettle reactor was heated by circulating hot water to 72°C.  $\text{N}_2$  inlet was opened into the reactor. KPS, 0.5 g, was added into the reactor (equivalent to 0.112 pphm) and held for 5 min. Then, 25.8 g of the monomer emulsion above (4 wt % of monomer emulsion) was added into the reactor. With the exotherm taken into account, the batch temperature was adjusted and maintained at 80°C. After holding for 10 min, both the remaining monomer emulsion and initiator solution were fed slowly into the reactor as two separate delays. For the monomer emulsion, the feed delay time was 180 min (i.e., 3.44 g/min feed rate) and for the initiator solution, the feed delay was 210 min (0.2 g/min feed rate). After all the initiator had been added, the reaction was continued for 60 min (cook-out) to decrease the residual monomer.  $\text{NH}_4\text{OH}$ , 2.25 g (26% concentration), in 2.25 g DI water was added into the reactor to increase the pH to enhance the latex shear and shelf stability. The batch was then cooled to below 40°C, and 0.7 g of biocide (Kathon LX, 1.5% active) was

added. The total solid content was 51.4%. Residual monomer was measured using GC/MS and typically was about 0.5–1% based on the wet-latex weight. The surfactant level used was 4.51 pphm. When V-50 (Wako Chemical) was used in place of KPS as an initiator, the reaction temperature was kept at 60°C.

### Preparation of Acrylic PSA Using Semicontinuous Solution Polymerization

#### Preparation of Monomer Mixture

Five hundred fifty-seven grams of 2EHA (or BA) was mixed with 14.3 g of AA and 1.36 g of Vazo 67 (AIBN) using magnetic stirrer at room temperature (RT) for 20 min.

#### Preparation of Catalyst Solution

Seventy grams of toluene was mixed with 0.62 g of Vazo 67 using magnetic stirrer at RT.

#### Polymerization Procedure

Two hundred eighty-two grams of hexane was added into a 1-L glass kettle reactor and heated to reflux at 68°C. One hundred forty-three grams of monomer mixture as prepared above was added into the reactor and the reaction was run for 1 h at 73°C. After 1 h, the remaining monomer mixture was added slowly at 1.3 g/min for 30 min and then increased to 2.17 g/min for 180 min. The total monomer feed delay was 210 min. The reaction was continued for 1 h after the monomer feed delay had been completed. Catalyst solution was then added slowly over a 1-h period (1.2 g/min). After the catalyst solution delay was completed, the reaction was continued for 1 h. Then, 243 g of toluene and 12.56 g of isopropanol were added as diluent. The total theoretical solid was 48.5% and the total amount of catalyst used was 0.346 pphm. The residual monomer determined by GS/MS was  $\approx 1.2\%$  based on solution weight. Al acetyl acetonate crosslinker in toluene/isopropanol 1:3:9 by weight ratio (7.7 wt % Al acetyl acetonate in solution) was post added to the polymer solution at 0.3–1 wt % based on solid to achieve the desired gel contents. The mixture was placed in a roller for 3 h to ensure even mixing before casting the film.

#### PSA Testing

Emulsion PSAs were coated using wire-rod die directly onto 50-micron polyethylene terephtha-

late (PET) (MYLAR®) to give a 30-micron dry film thickness. For solution PSAs, knife-over-roll die was used to give 30-micron dry film thickness.

A standard drying temperature of 121°C for 10 min was used to dry the emulsion and solution film, unless it was otherwise indicated.

PSA testing was done at 23°C and 50% relative humidity and the samples were climatized into this condition 24 h before testing.

Loop tack and 90° peel were done off stainless steel and high density polyethylene substrates. The test methods were in accordance with the Pressure Sensitive Tape Council no. 7 procedure, and they were described in detail previously.<sup>10</sup> Shear holding power was done off stainless steel using a 1.27 × 1.27 cm PET-coated strip and 4.9N hanging weight according to Pressure Sensitive Tape Council no. 7, as described previously.<sup>10</sup>

### Viscoelastic Characterization

Rheometrics® RDA II was used to study the PSA film viscoelastic properties. DMA measurements were done by heating the samples at 3°C/min, and by oscillating at 10 rad/s. The geometry used was 8-mm diameter parallel plates with 1.5-mm sample thickness at the starting temperature (−80°C). PSA films were prepared by direct coating onto siliconized paper, drying them in the oven at 121°C for 10 min, and plying them up to build thickness.

### Solvent Extraction and Swelling

Determination of gel content and swelling were done using the membrane gel partitioning method. Unlike the Soxhlet extraction, this method does not require heat and hence it reduces the possibility of further crosslinking of the sample. For gel content determination, approximately 60 mg of adhesive film that was weighed accurately using microbalance was placed between two PTFE-coated papers having 10-μm pore size and 47-mm diameter. The pouch was then heat sealed and placed inside a 22-mL glass scintillation vial with a plastic seal cap. Fifteen milliliters of tetrahydrofuran (THF) was added into the vial and the cap was sealed. The vial was tumbled slowly end-to-end for 16 h. Triplicate samples were used. After 16 h, the swollen pouch was dried under the hood for 3 h followed by oven drying at 100°C for 2 h. At this time, the dried weight was measured. The gel content was calculated as the (dried weight/initial weight) × 100%.

The THF soluble fraction was saved for gel permeation chromatography (GPC) analysis.

For determination of average molecular weight between crosslink points ( $M_c$ ), 100% insoluble material must be swollen in a solvent. To obtain adhesive gel fraction of sufficient quantity to perform swelling experiment, 3 g of adhesive film was immersed in 300 g THF and shaken for 48 h. The slurry was then poured through a cellulosic timble in a Soxhlet apparatus without applying any heat to recover the gel fraction. The gel was dried at 25°C for 24 h under vacuum followed by drying at 40°C for 3 h under vacuum. Approximately 60 mg of adhesive gel was weighed accurately and placed between PTFE-coated paper having 5-μm pore size and 47-mm diameter. The pouch was heat sealed and placed in a 22-mL scintillation glass vial with a plastic seal cap. Fifteen milliliters of toluene was added in the vial and the sealed vial was tumbled end-to-end for 22 h. Triplicate samples were used. After 22 h, the swollen pouch was removed and immersed in liquid N<sub>2</sub>. The frozen pouch was weighed in microbalance by recording the first number that remained unchanged, i.e., when surface evaporation of liquid N<sub>2</sub> had been completed. The weight fraction of polymer ( $W_p$ ) in toluene was calculated as:

$$W_p = \frac{\text{weight of dry gel}}{\text{weight of swollen gel}} \quad (1)$$

and the volume fraction of polymer ( $\phi$ ) in toluene was calculated as:

$$\phi = \frac{W_p \rho_s}{W_p \rho_s + W_s \rho_p} \quad (2)$$

where  $W_s$  is the solvent weight fraction, i.e.,  $1 - W_p$ ,  $\rho_s$  is the density of toluene (0.8669 g/cm<sup>3</sup>), and  $\rho_p$  is the density of the dry polymer.  $\rho_p = 1.06$  g/cm<sup>3</sup> for P(*n*BA) and 0.99 g/cm<sup>3</sup> for P(2EHA). The Flory-Rehner equation was used to calculate  $M_c$ <sup>13</sup>:

$$M_c = \frac{V_1 \rho_p [\phi^{1/3} - \phi/2]}{-[\ln(1 - \phi) + \phi + \chi \phi^2]} \quad (3)$$

where  $V_1$  is molar volume of toluene (106.3 cm<sup>3</sup>/mol), and  $\chi$  is polymer-solvent interaction parameter. If  $\chi$  is not known, it can be estimated as follows<sup>14</sup>:



$$\chi = 0.34 + \frac{V_1}{RT} (\delta_1 - \delta_2) \quad (4)$$

where  $\delta_1$  is the solubility parameter of the polymer and  $\delta_2$  is the solubility parameter of toluene. The constant 0.34 is a fudge factor to account for the large difference in free volume between polymer and solvent.<sup>14</sup> For P(*n*BA),  $\delta_1 = 8.9$  (cal/cm<sup>3</sup>)<sup>1/2</sup>, for P(2EHA),  $\delta_1 = 8.6$  (cal/cm<sup>3</sup>)<sup>1/2</sup>, and  $\delta_2 = 8.9$  (cal/cm<sup>3</sup>)<sup>1/2</sup> for toluene.<sup>15</sup>

### Molecular Weight Characterization

The THF soluble fraction from the adhesive extraction experiment described above was taken from the scintillation vials and filtered through a 0.45- $\mu$ m Teflon membrane syringe filter. For solution polymerized acrylic PSAs, the solution was diluted further with THF to 0.22% solid. GPC set up with three columns using 5- $\mu$ m polystyrene particles was used to separate molecular weights. The apparatus (Water Alliance 2690) was equipped with refractive index detector (Water 410) and data system (Water Millennium 32).

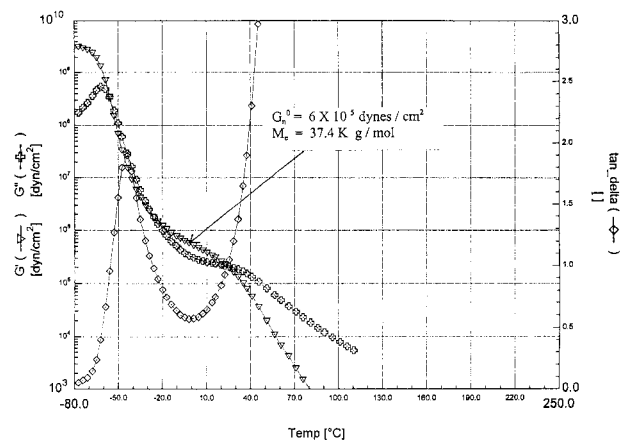
### Characterization of Emulsion Shear Stability

The colloidal shear stability was evaluated by using a Haake HS-I rheometer. The geometry used was coaxial cylinders with a rotating inner cylinder. The diameter of the outer cylinder was 20 mm and the inner cylinder was 19.950 mm. Therefore, the gap where the latex was placed was 0.025 mm. The shear rates used in evaluating the shear stability were 0 to  $4 \times 10^4$  s<sup>-1</sup> performed in two up-and-down cycles. The degree of thixotropic loss was related to the colloidal shear stability.

## RESULTS AND DISCUSSION

### $M_e$ of Acrylic PSAs

$M_e$  is one of the most critical molecular parameters influencing PSA performance. Unfortunately, the reported  $M_e$  of P(2EHA) and P(*n*BA), which both are the bases of commercial acrylic PSAs, had shown large discrepancies. For examples,  $M_e$  of P(2EHA) varies between 35,000<sup>16</sup> to 130,000<sup>17</sup> g/mol whereas  $M_e$  of P(BA) varies between 17,000<sup>16</sup> to 26,000<sup>9,17</sup> g/mol. The large discrepancies were caused by polydispersity effect where low molecular weight species act as plasticizer that increases  $M_e$ . In P(2EHA), assessment



**Figure 1** DMA of monodisperse poly(2-ethylhexyl acrylate).  $M_w = 241,800$  g/mol, PDI = 1.13.

of rubbery plateau modulus ( $G_n^o$ ) was less certain because the glass transition region was so broad that  $G_n^o$  was not easily defined.<sup>17</sup>

Because of the reasons mentioned above, calculation of  $M_e$  for the polydisperse sample must start from DMA characterization of monodisperse polymer. Figure 1 shows temperature sweep DMA of monodisperse P(2EHA). As shown in Figure 1,  $G_n^o$  could easily be determined from the location where  $\tan \delta$  was minimum following the prominent peak.  $M_e$  could then be calculated as:

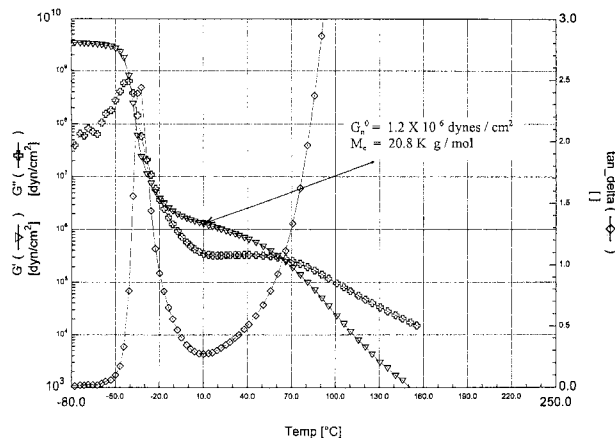
$$M_e = \frac{\rho_p R T}{G_n^o} \quad (5)$$

where  $\rho_p$  is the density of polymer,  $R$  is the gas constant ( $8.31 \times 10^7$  dyne-cm/mol $^\circ$ K) and  $T$  is the absolute temperature for the onset of rubbery plateau. Using eq. (5),  $M_e$  for monodisperse P(2EHA) was calculated to be 37,432 g/mol. Similarly, as shown in Figure 2,  $M_e$  for P(*n*BA) was calculated to be 20,773 g/mol.

Knowing  $M_e$  for monodisperse sample,  $M_e$  for polydisperse sample could be estimated from the plasticizer model<sup>12</sup>:

$$M_{e,\text{polydisperse}} = \frac{M_{e,\text{monodisperse}}}{\phi^{2.3}} \quad (6)$$

For gel-free polydisperse samples,  $\phi$  could easily be determined as the weight fraction of polymer species having molecular weight greater than the  $M_e$  for monodisperse sample. As shown in Figure 3, the GPC cumulative molecular weight distribu-

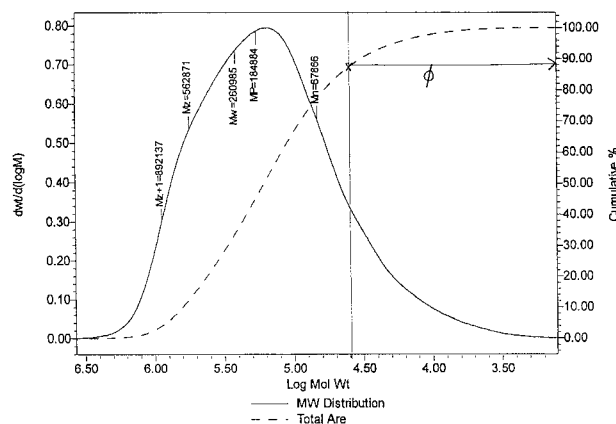


**Figure 2** DMA of monodisperse poly(*n*-butyl acrylate).  $M_w = 263,000$  g/mol, PDI = 1.16.

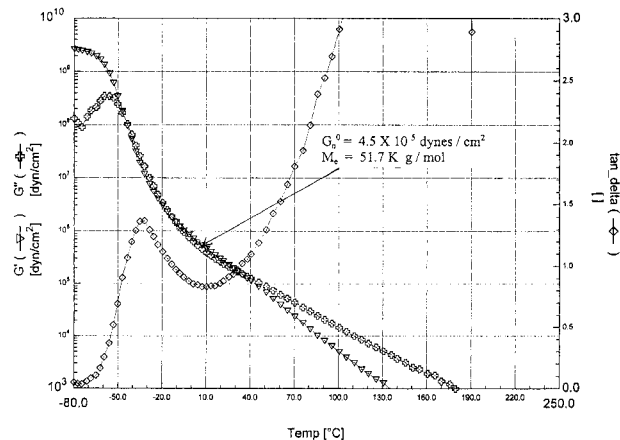
tion curve could be conveniently used to determine  $\phi$ .

For gel containing polydisperse sample, the gel content and molecular weight between crosslink points ( $M_c$ ) would need to be known before calculating  $\phi$ . If the sample contains gel having  $M_c \geq M_e$ , then the gel fraction must be included as high molecular weight polymer added together with the high molecular weight fraction of the sol polymer. As will be shown below, acrylic emulsion PSAs based on P(2EHA-*stat*-AA) and P(BA-*stat*-AA) contained gel of this type. However, if the sample contains gel having  $M_c < M_e$ , i.e., highly crosslinked network, then the gel fraction acts as filler and therefore need not be included in calculating  $\phi$ .

Figure 4 shows the temperature sweep DMA of



**Figure 3** GPC molecular weight distribution and cumulative curves of polydisperse P(2EHA-*stat*-AA) 97.5/2.5 by weight made by solution polymerization.



**Figure 4** DMA of polydisperse P(2EHA-*stat*-AA) 97.5/2.5 by weight made by solution polymerization.

polydisperse gel-free P(2EHA-*stat*-AA) 97.5/2.5 by weight made by solution polymerization.  $M_e$  was directly calculated from  $G_n^0$  value of  $4.5 \times 10^5$  dyne/cm<sup>2</sup> using eq. (5). This DMA determined  $M_e$  was found to be 51,706 g/mol. The predicted  $M_e$  from eq. (6) using  $\phi = 0.88$  from the GPC data (Fig. 3) was found to be 50,226. Hence, excellent agreement was found between the DMA determined  $M_e$  and that predicted from the plasticizer model. Table I shows the  $M_e$  of various gel-free acrylic solutions and emulsion PSAs determined from DMA data versus those predicted from the plasticizer model. Again, the agreement is excellent. In one example in which the  $M_w < 2 M_e$ ,  $M_e$  could not be obtained from the DMA data because the sample did not have a rubbery plateau region. The predicted  $M_e$  from the plasticizer model is therefore a hypothetical value indicating what the  $M_e$  would be for the given amount of low molecular weight species.

Table II shows the DMA determined  $M_e$  versus those predicted from the plasticizer model for crosslinked PSAs having various gel content. It appears that the predicted  $M_e$  from the plasticizer model were slightly lower than those calculated directly from the DMA data. The reason could be because of the uneven distribution of the low molecular weight species inside and outside the network. In emulsion polymerization performed using the semicontinuous process, the highest molecular weight species were formed early in the seed and the lower molecular weight species were formed during the feed delay and notably during cook-out.<sup>4</sup> Higher molecular weight species had higher probability to form crosslinking via hydrogen abstraction of the tertiary carbon atoms due

**Table I Entanglement Molecular Weight ( $M_e$ ) of Gel-Free Acrylic PSAs**

Polymers <sup>a</sup>	$M_w$ (g/mol)	$M_n$ (g/mol)	$\phi$	$M_e$ , Expt <sup>b</sup> (g/mol)	$M_e$ , Predicted <sup>c</sup> (g/mol)
Solvent borne					
P(2EHA-stat-AA)	214K	57K	0.88	52K	51K
P(BA-stat-AA)	271K	75K	0.97	23K	22K
Emulsion <sup>d</sup>					
P(2EHA-stat-AA)	88K	28K	0.62	e	112K
P(BA-stat-AA)	97K	30K	0.82	24K	29K
P(2EHA-stat-AA)	193K	38K	0.80	59K	62K
P(2EHA-stat-AA)	210K	50K	0.88	47K	50K
P(BA-stat-AA)	285K	47K	0.92	23K	25K
P(BA-stat-AA)	308K	98K	0.98	21K	21K

<sup>a</sup> All polymers contained 2.5 wt % AA.

<sup>b</sup>  $M_e = \rho RT/G_n^o$ , where  $G_n^o$  was obtained from DMA.

<sup>c</sup>  $M_e = (M_e, \text{monodisperse})/\phi^{2.3}$ , where  $\phi$  was obtained from GPC.

<sup>d</sup> Various levels of  $n$ -DDM were added to obtain gel-free latices.

<sup>e</sup> No  $G_n^o$  could be obtained from DMA because  $M_w \ll 2 M_e$ .

to higher number of these sites per chain.<sup>4</sup> In solvent-borne acrylic PSA, the broad polydispersity might be implicated to favor lowest molecular weight species to partition preferentially toward lower molecular weight species after film formation. Subsequently, as crosslinking reaction took place, the highest molecular weight species would be most efficiently forming network and the lowest molecular weight species would partition more toward the sol polymer.

The  $M_e$  for monodisperse P(2EHA) was  $2 \times M_e$  for monodisperse P( $n$ BA). This means that P(2EHA) is more capable of forming fibrils during peeling or debonding.<sup>9</sup> Figures 5 and 6 show the frequency sweep master curves of monodisperse P(2EHA) and P( $n$ BA) shifted to a reference tem-

perature of 25°C. The  $G'$  at 1 rad/s which corresponds to the bonding frequency<sup>7,8</sup> of P(2EHA) was 1 order of magnitude lower than that of P( $n$ BA), although both polymers had the same molecular weights. This is because of lower entanglement density in P(2EHA) as demonstrated by a lower  $M_w/M_e$  ratio. The ratio of  $G''$  at 437 rad/s to  $G'$  at 1 rad/s for P(2EHA) and P( $n$ BA) were found to be 40 and 1.43, respectively. This means that P(2EHA) gives higher peel than that of P( $n$ BA) if all of the other molecular parameters are equal, as will be shown below. Chang<sup>7</sup> and Yang and Chang<sup>8</sup> reported that higher  $G''/G'$  gave higher peel in PSA. The contribution of lower  $G'$  at 1 rad/s for P(2EHA) led to higher loop tack compared with that for P( $n$ BA), as will be shown

**Table II Entanglements Molecular Weight ( $M_e$ ) of Crosslinked Acrylic PSAs**

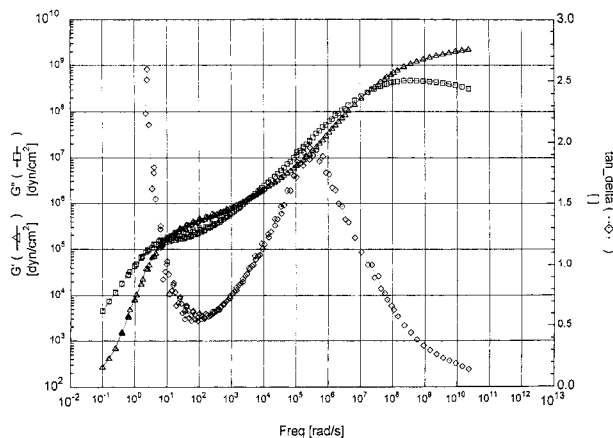
Polymers <sup>a</sup>	Gel Content (%)	$M_c$ (g/mol)	$\phi$	$M_e$ , Expt <sup>b</sup> (g/mol)	$M_e$ , Predicted <sup>c</sup> (g/mol)
Solvent borne <sup>d</sup>					
P(2EHA-stat-AA)	71	61K	0.88	55K	50K
P(BA-stat-AA)	80K	63K	0.96	25K	23K
Emulsion					
P(2EHA-stat-AA)	78	54K	0.95	48K	42K
P(BA-stat-AA)	79	80K	0.99	28K	22K
P(2EHA-stat-AA)	32	53K	0.80	67K	64K
P(BA-stat-AA)	52K	80K	0.98	25K	21K

<sup>a</sup> All polymers contained 2.5 wt % AA.

<sup>b</sup>  $M_e = \rho RT/G_n^o$ , where  $G_n^o$  was obtained from DMA.

<sup>c</sup>  $M_e = (M_e, \text{monodisperse})/\phi^{2.3}$ , where  $\phi$  was obtained from GPC and gel content.

<sup>d</sup> 1 wt % Al-acetyl-acetonate was added into P(2EHA-stat-AA) and 0.75 wt % was added into P(BA-stat-AA).



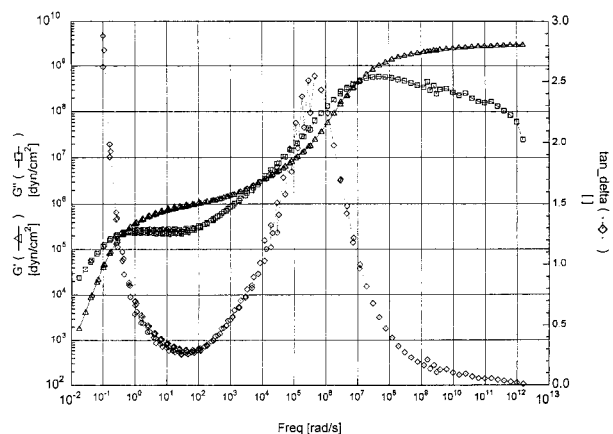
**Figure 5** DMA mastercurves of monodisperse poly(2-ethyl hexyl acrylate).  $M_w = 241,800$  g/mol at 25°C. Note:  $[G'' \text{ at } 437 \text{ rad/s}]/[G' \text{ at } 1 \text{ rad/s}] = 40$ .

below. Chang<sup>7</sup> and Yang and Chang<sup>8</sup> reported the inverse proportionality between loop tack and  $G'$ .

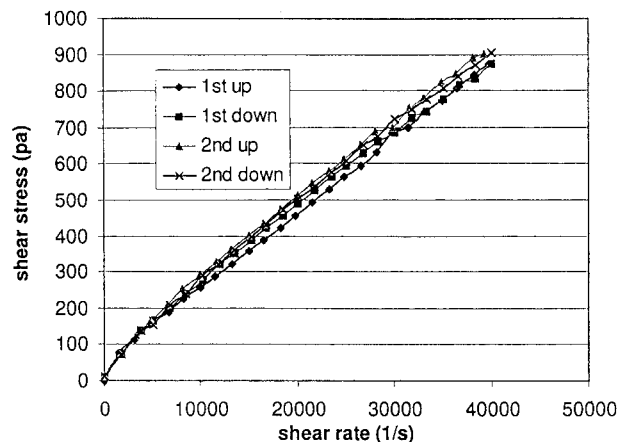
#### Effect of Emulsion Polymerization Condition on Adhesive Performance

Synthesis of *n*BA using semicontinuous emulsion polymerization process led to branching and crosslinking.<sup>4</sup> The extent of these depended on the polymerization temperature and the catalyst used.

Model emulsions based on P(2EHA-stat-AA) and P(*n*BA-stat-AA) at 97.5/2.5 weight ratio were prepared using semicontinuous emulsion polymerization under a monomer-starved condition. Two different thermal initiators were used. When KPS was used, the polymerization temperature



**Figure 6** DMA mastercurves of monodisperse poly(*n*-butyl acrylate).  $M_w = 263,000$  g/mol at 25°C. Note:  $[G'' \text{ at } 437 \text{ rad/s}]/[G' \text{ at } 1 \text{ rad/s}] = 1.43$ .

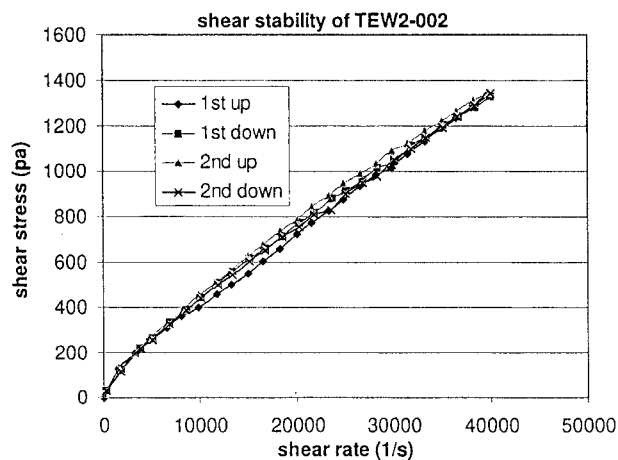


**Figure 7** Shear stability of emulsion P(*n*BA-stat-AA) 97.5/2.5 by weight.

was 80°C. When Wako V-50 was used, the polymerization temperature was 60°C.

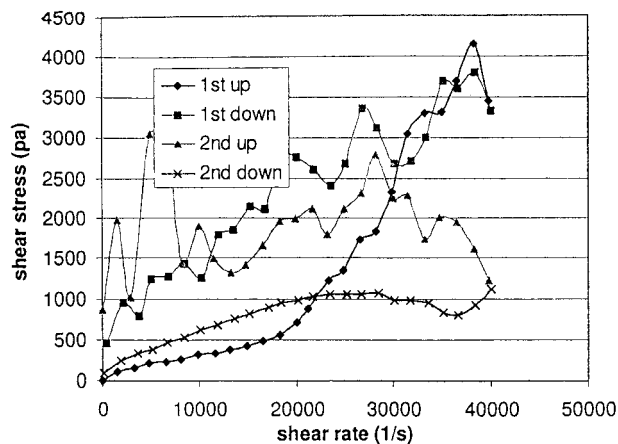
The use of 2.5 wt % AA in the acrylic copolymer was needed to obtain good colloidal shear stability. Figures 7–9 show shear stress versus shear rate curves from 0 to 40,000 s<sup>-1</sup> up and down two cycles of P(BA-stat-AA), P(2EHA-stat-AA), and P(2EHA), respectively. It is clear that from Figure 9, P(2EHA) without AA copolymer had poor shear stability. Shear induced coagulation was apparent because the curves showed erratic behavior with large thixotropic loss and shear thickening. AA copolymer was reported to give electro-steric stabilization in acrylic lattices.<sup>18</sup>

The changes in molecular weight and the microgel formation for the two different initiators and base polymers followed at various reaction



**Figure 8** Shear stability of emulsion P(2EHA-stat-AA) 97.5/2.5 by weight.





**Figure 9** Shear stability of emulsion P(2EHA). Note: the absence of AA caused poor shear stability.

times are shown in Table III. Because the reaction was run under a monomer-starved condition, the polymer concentration in the latex particles was high at all times and as a result, microgels were formed early. As the reaction proceeded, the formation of microgel increased and molecular weight of the THF-soluble fraction decreased. This is expected because higher molecular weight species was the most prone for hydrogen abstraction and chain transfer because of higher number of tertiary carbon atoms per chain. As shown in Table III, V-50 initiator yielded higher molecular weight polymers with lower gel contents compared with those made by using KPS. Lower reaction temperature used in V-50 initiated system might lower the chain transfer to polymer rate constant,<sup>4</sup> resulting in lower gel content and higher molecular weight.

Table III also shows that molecular weights (notably  $M_w$ ) of P(BA-stat-AA) were higher than those of P(2EHA-stat-AA). This finding is not unique to the emulsion polymerized system only. Examination of the solvent-borne polymers, as shown in Table I, also reveals the same finding. It is postulated that the lower molecular weight in P(2EHA-stat-AA) was caused by higher chain transfer to monomer by the propagating radicals. Rätzsch and Zschach<sup>19</sup> reported the chain transfer to monomer constant of P(2EHA) radical to be 2–3 times higher than that of P(ethyl acrylate).

Table IV shows the molecular and adhesive properties of the final batches of P(2EHA-stat-AA) and P(BA-stat-AA) made by semicontinuous emulsion polymerization using KPS and V-50 initiators. Both loop tack and peel of P(2EHA-stat-AA) were higher than those of P(BA-stat-AA)

whereas the shear was lower. This is expected because the  $M_e$  of P(2EHA-stat-AA) were approximately twice of P(BA-stat-AA). As discussed above,  $G''/G'$  ratio of P(2EHA) was 1 order of magnitude higher than that of P(BA). Hence, P(2EHA) would dissipate higher viscoelastic energy during debonding. Shear holding power, unlike peel and loop tack, is directly proportional to zero-shear viscosity at room temperature, which in turns is influenced by entanglement and crosslinking.<sup>5</sup> The higher the entanglement and crosslinking densities are, the higher the zero-shear viscosity, and hence the higher the shear holding power. In Table IV, the ratio of  $M_w/M_e$  for P(2EHA-stat-AA) ranged from 3.5 to 5 whereas that for P(BA-stat-AA) ranged from 12 to 33. It is important to note that very high  $M_w/M_e$  ratio such as that shown in P(BA-co-AA) prepared using V-50 initiator at 60°C, reduced the loop tack and peel significantly. This reduction could be worsened further by the higher  $M_n$  which means that there were less low molecular weight species available to plasticize the polymer which decreased the viscoelastic energy dissipation. Despite the much higher  $M_w/M_e$ , P(BA-stat-AA) pre-

**Table III**  $M_w$  Changes and Microgel Formation during Semicontinuous Emulsion Polymerization ( $M_w$  and  $M_n$  Applied to the THF-Soluble Fractions)

$R_{xn}$	Time (h)	Gel Content (%)	$M_w$ (g/mol)	$M_n$ (g/mol)
P(2EHA-stat-AA) 97.5/2.5, KPS initiated at 80°C				
	1	64	195,000	65,100
	2	69	163,000	35,000
	3	79	153,000	35,100
	4 $\frac{1}{2}$	79	148,000	32,000
P(BA-stat-AA) 97.5/2.5, KPS initiated at 80°C				
	1	72	496,000	118,000
	2	77	432,000	97,800
	3	78	343,000	61,400
	4 $\frac{1}{2}$	79	257,000	45,500
P(2EHA-stat-AA) 97.5/2.5, V-50 initiated at 60°C				
	1	58	237,000	56,000
	2	60	296,000	39,000
	3	63	244,000	40,000
	4 $\frac{1}{2}$	64	234,000	28,000
P(BA-stat-AA) 97.5/2.5, V-50 initiated at 60°C				
	1	5	930,000	150,000
	2	5	780,000	125,000
	3	35	695,000	120,000
	4 $\frac{1}{2}$	40	691,000	120,000

**Table IV Molecular and Adhesive Properties of Acrylic Emulsion PSAs (PSAs Were Coated on 50- $\mu$ m PET at 30- $\mu$ m Dry-Film Thickness)**

I. KPS initiated at 80°C					
Composition <sup>a</sup>	Gel Content (%)	$M_c$ (g/mol)	$M_e$ (g/mol) <sup>b</sup>	$M_w$ (g/mol)	$M_n$ (g/mol)
P(2EHA-stat-AA)	78	54K	42K	148K	32K
P(BA-stat-AA)	79	80 k	21 k	257 k	45 k
	Loop Tack Stainless Steel (N/m)	Loop Tack HDPE (N/m)	90° Peel Stainless Steel (N/m)	90° Peel HDPE (N/m)	Shear (min)
P(2EHA-stat-AA)	368	228	228	105	27
P(BA-stat-AA)	316	175	158	70	70
II. V-50 <sup>®</sup> initiated at 60°C					
Composition	Gel Content (%)	$M_c$ (g/mol)	$M_e$ (g/mol) <sup>b</sup>	$M_w$ (g/mol)	$M_n$ (g/mol)
P(2EHA-stat-AA)	62	93K	47K	234K	28K
P(BA-stat-AA)	42	100K	21K	691K	120K
	Loop Tack Stainless Steel (N/m)	Loop Tack HDPE (N/m)	90° Peel Stainless Steel (N/m)	90° Peel HDPE (N/m)	Shear (min)
P(2EHA-stat-AA)	351	193	228	123	16
P(BA-stat-AA)	88	35	123	53	30

<sup>a</sup> All compositions contained 2.5 wt % AA.<sup>b</sup> Calculated from the plasticizer model.

pared by V-50 initiator showed lower shear than that of P(BA-stat-AA) prepared by KPS. Lower gel contents were responsible for the lower shear.

#### Effect of Molecular Weight on Adhesive Performance

Both peel and loop tack are measures of adhesive performance which depend significantly on viscous flow during bonding and viscoelastic energy dissipation during debonding. The only differences between peel and loop tack are the contact time and contact force. In peel, 20-min dwell time after application force of 4 lbs. was given, whereas in loop tack, separation began after only 1-s contact time and the contact force was given by the bending force of 50  $\mu$ m PET film ( $\sim$ 10 g). Because both tack and peel are the outcome of viscoelastic processes, they bear direct relationship to the molecular weight of the polymer and its entanglement.

Table V shows the effect of molecular weights as represented by  $M_w$ ,  $M_n$ , and  $M_e$  (weight average, no average, and entanglement average) on adhesive performance. Different levels of chain transfer agent, *n*-DDM (0.1 – 0.5 wt %), was added to provide gel-free emulsion PSA compositions. One solution acrylic each, based on P(2EHA-stat-AA) and P(*n*BA-stat-AA), were also evaluated as comparison, and they are shown in Table VI.

As shown in Table V, P(2EHA-stat-AA) composition showed higher peel and loop tack than those for P(*n*BA-stat-AA) consistent with the finding for crosslinked emulsion PSAs shown in Table IV. This follows the previous discussion in which higher  $M_e$  for P(2EHA) gave higher viscoelastic energy dissipation during debonding and higher viscous flow during bonding. Table V shows also the importance of  $M_w$  in influencing tack and peel. Very low  $M_w$  compositions, although they

**Table V Effect of Molecular Weight on Adhesive Properties of Gel-Free Compositions (PSAs Were Coated on 50- $\mu$ m PET Film at 30- $\mu$ m Dry-Film Thickness)**

$M_w$ (g/mol)	$M_n$ (g/mol)	$M_e$ (g/mol)	Tack SS (N/m)	Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	4.9N $\times$ 1.27 $\times$ 1.27 cm Shear (min)
P(2EHA-stat-AA) 97.5/2.5							
87.8 K	27.8K	112K <sup>a</sup>	107	93	53	51	$\leq 0.1$
201 K	47K	59K	824	702	351	193	0.3
246 K <sup>+</sup>	54K <sup>b</sup>	57K	1175	842	596	246	0.3
420 K	67K	47K	965	298	649	211	1.3
P(BA-stat-AA) 97.5/2.5							
97.3 K	30.5K	29K	179	191	91	97	$\leq 0.1$
285 K	47.3K	23K	731	268	470	146	1.8
271 K <sup>+</sup>	75.5K <sup>b</sup>	22K	772	354	652	109	2
310 K	90K	21K	481	207	698	147	3.7

<sup>a</sup> Calculated from  $M_e = 37.4/(0.62)^{2.3}$ . 37.4 K is  $M_e$  for monodisperse polymer and 0.62 is the vol fraction of species with mol wts  $\geq 37.4$  K.  $G_n^*$  for this sample could not be measured because  $M_w \ll 2 M_e$ .

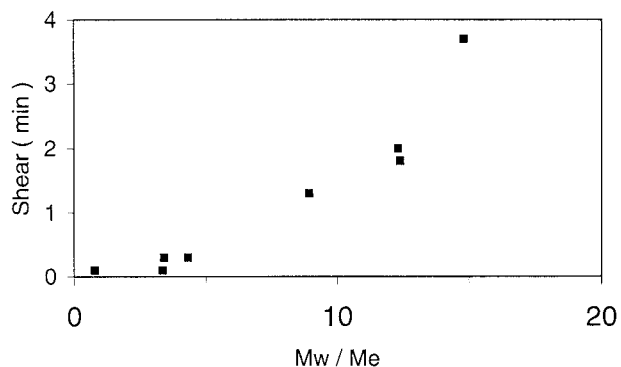
<sup>b</sup> Solvent-borne acrylic PSA. Others are emulsion.

gave high viscous flow because of plasticization effect, did not give high viscoelastic energy dissipation during debonding because the filament would fracture very quickly because of lack of entanglement.<sup>6</sup> Therefore, the peel and loop tack of very low  $M_w$  compositions were much lower. As  $M_w$  was increased, peel and loop tack were increased up to  $M_w/M_e$  ratio of  $\sim 10$  and then, further increase in  $M_w$  caused a decrease in loop tack. This is expected because very high  $M_w$ , especially when  $M_n$  is also high, give less viscous flow during bonding and more elastic response

during debonding. During debonding, to obtain high viscoelastic energy dissipation, the bulk adhesive force should not be higher than the interfacial force at the adhesive-substrate boundary to avoid premature interfacial debonding. The interfacial force here is referred to both viscoelastic and thermodynamic forces at the boundary layer.<sup>20</sup> Hence, high viscoelastic energy dissipation can only be obtained if there is good anchorage of the adhesive onto the substrate and low modulus-high elongation fibrils that are deformed during the peeling process.

**Table VI Effect of Gel Content on Adhesive Properties (PSAs Were Coated on 50- $\mu$ m PET Film at 30- $\mu$ m Dry-Film Thickness)**

Gel Content (%)	$M_c$ (g/mol)	$M_w$ (g/mol)	$M_n$ (g/mol)	$M_e$ (g/mol)	L. Tack SS (N/m)	L. Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	4.9N $\times$ 1.27 $\times$ 1.27 cm Shear (min)
1. P(2EHA-stat-AA) 97.5/2.5 emulsion									
77	53K	142K	38K	42K	368	228	228	93	27
32	51K	124K	32K	63K	614	421	684	175	2.4
2. P(BA-stat-AA) 97.5/2.5 emulsion									
79	80K	257K	46K	21K	316	175	158	70	70
52	80K	230K	60K	21K	386	228	210	88	14
3. P(2EHA-stat-AA) 97.5/2.5 solution									
71	61K	70K	24K	50K	228	175	105	53	761
27	65K	240K	47K	54K	824	316	719	193	25
4. P(BA-stat-AA) 97.5/2.5 solution									
80	63K	79K	30K	23K	246	123	105	53	5000
40	63K	230K	61K	23K	439	140	333	53	250



**Figure 10** Shear as a function of  $M_w/M_e$  ratio in gel-free acrylic PSAs.

In Table V, solvent-borne acrylic PSA compositions were inserted to show comparison against the emulsions. It is clear that solvent-borne acrylics (the third compositions in Table V) are not unique in terms of their peel and loop tack properties because their results are very much influenced by the molecular weight effect which fit well in Table V. This is to say that the surfactant used (nonyl phenol ethoxylate sulfate Polystep B-27) at 4.5 wt % level did not cause detrimental effect on adhesion. Nonyl phenol ethoxylate surfactant had been shown to be a plasticizing surfactant, which depending on the polymeric system and the level used, might not reduce the peel in emulsion PSA.<sup>20</sup> Polystep B-27 as 100% solid has a DSC-midpoint  $T_g$  of  $-8^\circ\text{C}$  and some finger tack.

Figures 10 and 11 show plots of shear and loop tack off stainless steel versus  $M_w/M_e$  ratio of various gel-free acrylic PSAs listed in Table V. As expected, the shear increased as this ratio was increased because of increase in zero shear viscosity. Loop tack, however, showed a maximum as this ratio was increased and then it decreased. This is consistent with the discussion above.

#### Effect of Gel Content on Adhesive Performance

Whereas molecular weight and molecular weight between entanglements affect peel and loop tack properties of acrylic PSAs, gel content and network morphology have a more pronounced effect on shear holding power.

As shown in Table VI, coated PSAs based on emulsion and solution polymerized acrylic polymers show dramatic decrease in shear holding power as the gel content is decreased. This is independent of the method of polymerization, i.e., solvent or emulsion. Shear holding power ( $T$ ) is

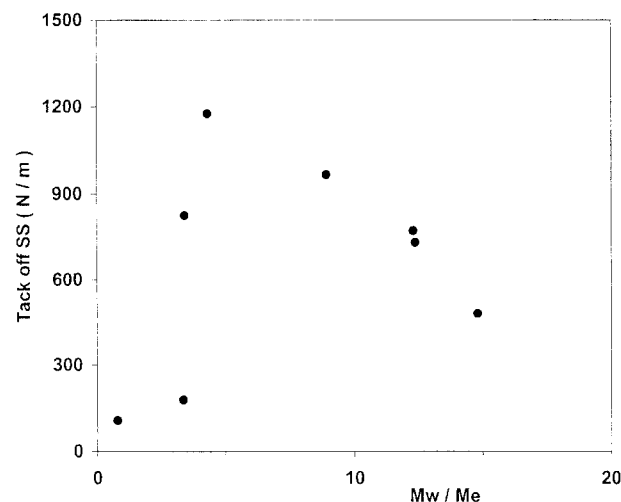
directly proportional to zero shear viscosity as given by the following equation<sup>21</sup>:

$$T = \frac{L^2 W \eta}{2tMg} \quad (7)$$

where  $T$  is time to failure,  $L$  is length of overlap,  $W$  is the width of the tape,  $\eta$  is zero shear viscosity,  $t$  is the adhesive thickness,  $M$  is the load, and  $g$  is gravitational constant. With everything else being constant, therefore shear holding power ( $T$ ) is directly influenced by the level of crosslinking (gel content), network morphology, and entanglement.

In all cases, P(*n*BA-stat-AA) compositions show higher shear holding power compared with that of P(2EHA-stat-AA) regardless of the method of polymerization. This effect is attributed to higher  $M_w/M_e$  ratio in P(BA-stat-AA), as discussed previously. It is also clear that as the gel content was decreased, the peel and loop tack were increased in both acrylic solution and emulsion PSAs. Uncrosslinked polymers having broad polydispersity ( $\text{PDI} \approx 3.5\text{--}5.5$ ) was effective in providing high viscoelastic energy dissipation during debonding. In contrast, network is considered elastic and does not dissipate high viscoelastic energy during debonding.

Finally, network morphology plays a significant role in influencing the shear holding power as well as its balance with peel and loop tack. As shown in Table VI, shear holding power of solution acrylic PSAs are 1 to 2 orders of magnitude



**Figure 11** Loop tack off stainless steel as a function of  $M_w/M_e$  ratio in gel-free acrylic PSAs.



**Table VII Conventional Emulsion Versus Solvent-Borne Acrylic PSAs**

Adhesive	L. Tack SS (N/m)	L. Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	4.9N × 1.27 × 1.27 cm Shear (min)
1. P(2EHA-stat-AA) 97.5/2.5, 75% gel					
Emulsion	370	226	205	93	25
Solvent	221	184	105	58	761
Tackified with 15% Snowtack® 920					
Emulsion	440	319	237	116	15
Solvent	491	300	211	98	250
2. P(BA-stat-AA) 97.5/2.5, 80% gel					
Emulsion	328	181	175	67	70
Solvent	249	121	107	46	5000
Tackified with 15% Snowtack 920					
Emulsion	433	233	217	81	55
Solvent	368	253	228	123	386

higher than that of the emulsions. As mentioned previously, microgels were formed during semi-continuous emulsion polymerization of 2-EHA and BA and their morphology could be retained after film formation. In contrast, solvent-borne acrylic started with gel-free composition, which following solvent evaporation, would begin to undergo crosslinking in the film because of reaction between the AA and Al acetyl acetate. It is hypothesized that the resulting network morphology would be continuous. In short, discrete network morphology found in acrylic emulsion PSA gave much lower shear compared with continuous network morphology found in acrylic solution PSA. Table VII shows a summary of adhesive performance for emulsion versus solvent-borne acrylic having the same gel content. The addition of 15 wt % tackifier reduced shear and increased peel and loop tack in both emulsion and solution acrylic PSAs. Tackifier increased  $M_e$  and  $T_g$  which favors viscoelastic energy dissipation during debonding and viscous flow during bonding.<sup>6,7,10</sup> Following the previous discussion, tackifier addition would decrease zero shear viscosity and simultaneously increase the sol fraction which has the net effect of decreasing shear and increasing peel and loop tack.

#### Effect of High $T_g$ Copolymer on Adhesive Properties

Commercial acrylic PSAs normally contain high  $T_g$  copolymer such as methyl methacrylate, methyl acrylate, and vinyl acetate to improve shear holding power. These copolymers, unfortunately, also have low  $M_e$  and therefore have an

adverse effect in reducing peel and tack. Recently, high  $T_g$ -high  $M_e$  copolymer such as vinyl decanoate (EXXAR®) has been shown to increase shear holding power without reducing the peel and tack.<sup>16</sup> However, it is important to realize that increase  $T_g$  means lower low temperature adhesion which limits the commercial application of PSA from bonding at low temperature. From a fundamental standpoint, it is still unclear whether the improvement in shear obtained from having EXXAR might not be attributable to hydrogen bonding of the ether groups that would have increased cohesive strength of the adhesive and possibly even increased the interfacial energy on polar substrates.

In this section, the effect of copolymerizing 2-EHMA with 2EHA on adhesive performance will be shown. P(2-EHMA) differs from P(2EHA) in two aspects. First, P(2-EHMA) has a much higher  $T_g$  than that of P(2EHA). Second, the absence of tertiary vinyl carbon in P(2-EHMA) eliminates the chain transfer to polymer reaction that is prominent in P(2EHA) and P(*n*BA) emulsion polymerization performed in semicontinuous mode. However, this latter aspect is minimal when 2-EHMA is copolymerized with 2EHA and the copolymer microstructure is random. Because P(2-EHMA) and P(2EHA) have a similar structure, they should have a similar critical surface energy and  $M_e$ . Therefore, the objective here is solely to determine the effect of  $T_g$  on adhesive properties while holding everything else the same.

Table VIII shows adhesive properties of P(2EHA-stat-2-EHMA-stat-AA) made by semi-

**Table VIII** Effect of High  $T_g$  Copolymer on Adhesive Properties

P(2EHA-stat-2EHMA-stat-AA) Composition	$T_g$ (°C) <sup>a</sup>	L. Tack SS (N/m)	L. Tack		90° Peel		4.9N × 1.27 × 1.27 cm Shear (min)
			HDPE (N/m)	90° Peel SS (N/m)	HDPE (N/m)		
97.5-0-2.5 <sup>b</sup>	-38	316	228	246	105	15	
82.5-15-2.5 <sup>c</sup>	-32	351	281	246	88	23	
48.75-48.75-2.5 <sup>d</sup>	-17	526	263	298	123	120	
0-97.5-2.5 <sup>e</sup>	36	7	7	3.5	1.8	≥10 <sup>4</sup>	

<sup>a</sup> From tan  $\delta$  peak, DMA ran at 10 rad/s.

<sup>b</sup> Gel content = 78%,  $M_w$  = 161 K g/mol,  $M_n$  = 30 K g/mol.

<sup>c</sup> Gel content = 79%,  $M_w$  = 156 K g/mol,  $M_n$  = 40 K g/mol.

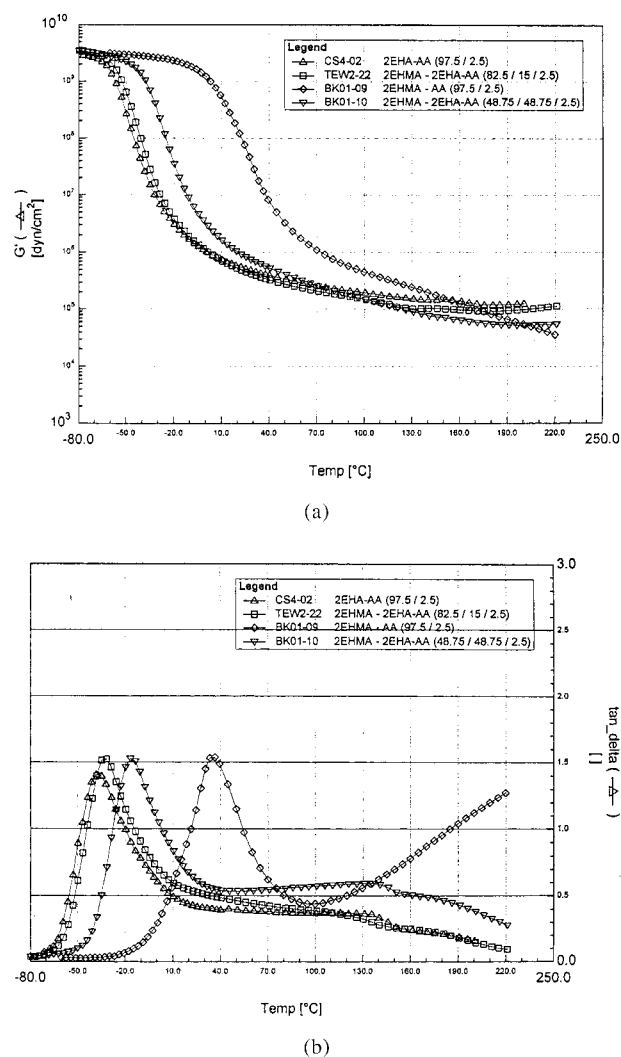
<sup>d</sup> Gel content = 74%,  $M_w$  = 230 K g/mol,  $M_n$  = 43 K g/mol.

<sup>e</sup> Gel content = 7%,  $M_w$  = 478 K g/mol,  $M_n$  = 142 K g/mol.

continuous emulsion polymerization using KPS as an initiator. Temperature sweep DMAs of various compositions are shown in Figure 12(a) and (b). As shown in Table VIII, appreciable impact on shear was obtained only after the  $T_g$  was raised by at least 20°C. P(2-EHMA-stat-AA) 97.5/2.5 showed very high shear because its complex modulus at 25°C ( $G^*$ ) was 2 orders of magnitude higher than P(2EHA-stat-AA) 97.5/2.5 as shown in Figure 12(a) and (b) [note:  $G^* = \sqrt{(G')^2 + (G'')^2}$  and  $G'' = G' \tan \delta$ ]. Shear holding power is directly proportional to zero shear viscosity which is directly proportional to  $G^*$ . However, because  $G'$  at 30°C (corresponding to bonding condition, i.e., 1 rad/s, via the WLF principle) for P(2-EHMA-stat-AA) 97.5/2.5 are  $3 \times 10^7$  dyne/cm<sup>2</sup>, the Dahlquist criteria for achieving intimate contact with the substrate was not met.<sup>5</sup> As a result, peel and loop tack of P(2-EHMA-stat-AA) 97.5/2.5 were very low. It is interesting to observe the increase in loop tack and peel off stainless steel for P(2EHA-stat-EHMA-stat-AA) 48.75/48.75/2.5 in addition to the increase in shear, which is expected because of increase in  $G^*$  compared with those of P(2EHA-stat-AA) 97.5/2.5. The incorporation of 2-EHMA as a comonomer brought higher molecular weights in addition to an increase in  $T_g$ . As discussed above, higher  $M_w$  gave higher loop tack and peel up to  $M_w/M_e \sim 10$  for the linear polymer. This is because of higher viscoelastic energy dissipation. Increased  $T_g$  led to higher  $G^*$  and hence higher zero shear viscosity at room temperature which increased shear holding power.

## CONCLUSIONS

Acrylic emulsion PSAs based on P(2EHA-stat-AA) and P(BA-stat-AA) 97.5/2.5 wt % showed sig-



**Figure 12** (a) Effect of high  $T_g$  copolymer on DMA properties of acrylic emulsion PSA. (b) Effect of high  $T_g$  copolymer on DMA properties of acrylic emulsion PSA.

nificantly lower shear holding power than that of their solvent counterparts. This difference was caused mainly by the discrete microgels that were connected by entanglements in contrast with the continuous network formed in acrylic solution PSA film.

Unlike shear holding power, loop tack and peel were mainly affected by molecular properties of the sol polymer in both emulsion and solution PSAs. Higher sol fraction led to increased loop tack and peel because of increased viscoelastic energy dissipation and more intimate contact with the substrate. The same reasoning and finding were applicable to higher entanglement molecular weight polymer, e.g., P(2EHA) versus P(*n*BA).

Increased  $T_g$  obtained by copolymerizing 2EHA with 2-EHMA could only moderately increase shear holding power if the difference in  $T_g$  was at least 20°C. From a technological consideration, this approach would have a detrimental effect in low temperature bonding.

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