

# Control of Structure and Tack Properties of Acrylic Pressure-Sensitive Adhesives Designed by a Polymerization Process

A. Aymonier,<sup>1</sup> D. Leclercq,<sup>1</sup> P. Tordjeman,<sup>2</sup> E. Papon,<sup>1</sup> J-J. Villenave<sup>1</sup>

<sup>1</sup>ERT "Chimie de l'Adhésion", LCPO (UMR 5629), ENSCPB, F 33607 PESSAC, Cedex, France

<sup>2</sup>LAIN CC 082, Université Montpellier 2, F 34095 Montpellier, Cedex 5, France

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**ABSTRACT:** Free radical emulsion polymerization of methyl methacrylate (MMA) and 2-ethylhexyl acrylate (EHA) results in the synthesis of pressure-sensitive adhesives (PSAs) with good tack properties. Management of both the copolymer composition and the polymerization process allows one to control the behavior of the PSA. Semicontinuous (SC) processes create polymer particles whose instantaneous composition is close to that of the feed particle. The SC Mixture process (continuous feeding with comonomer blends) affords nearly homogeneous latex particles and PSA films. The SC Gradient process (separate feedings at inversely varying rates) affords heterogeneous particles and films. The Batch process leads to somewhat heterogeneous films, but the hard (MMA-rich) microdomains are made compatible with their soft (EHA-rich) matrix because of the

assumed formation of tapered-type copolymers. Tack measurements indicate the importance of the particle and film structures. Too much hardness or softness leads to unacceptable lacks of adhesion and cohesion, respectively. Homogeneous structures prove adequate, but their tack properties collapse with rising temperature. Heterogeneous structures, with extensive phase segregation, prove unsatisfactory because they lack adhesion and cohesion. Finally, the association of well-balanced composition and compatible heterogeneity is the criterion for suitable PSA behavior. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2749–2756, 2003

**Key words:** emulsion polymerization; films; adhesion; structure–property relations

## INTRODUCTION

Pressure sensitive adhesives (PSAs) are widely used at the industrial scale as tapes, labels, or protective films.<sup>1</sup> From the basic research point of view, the tack property of such adhesives is a very interesting behavior. Tack is defined as the ability to instantaneously stick to a substrate under low pressure and be easily removed by adhesive separation (without leaving any residue at the substrate surface). Indeed, for viscoelastic materials to have the property of tack, adhesion must be developed during the bonding step and cohesion during the debonding step. To balance these conflicting properties, PSAs are generally based on complex formulations, including a polymer base that gives cohesion. Other additives, such as plasticizers and resins, improve mechanical and adhesive properties, respectively.<sup>2</sup> With the aim to better understand tack phenomenon, it is often decided to work with well-defined systems to initially lower the complexity of the system; for example, by direct macromolecular synthesis. On the nanoscopic (or macromolecular chain) scale, molecular weights ( $\bar{M}_{\text{macr}}$ ) and molec-

ular weights between entanglements ( $\bar{M}_{\text{macr};e}$ ) or crosslinks ( $\bar{M}_{\text{macr};c}$ ) have been proved to strongly influence tack. These parameters were investigated in many studies for acrylic copolymers. Creton et al.<sup>3</sup> studied the influence of ( $\bar{M}_{\text{macr}}$ ) on tack behavior of poly(*n*-butyl acrylate) synthesized by "living" anionic polymerization, Tobing et al.<sup>4</sup> synthesized and compared the tack of solvent-born or water-born PSAs with different ( $\bar{M}_{\text{macr};e}$ ) and ( $\bar{M}_{\text{macr};c}$ ), and Asua et al.<sup>5</sup> performed free-radical emulsion polymerization of acrylic monomers in the presence dodecyl mercaptan as a chain transfer agent (leading to  $7 \times 10^4 < \bar{M}_{\text{macr}} < 4 \times 10^5$  g/mol; i.e., 10 times lower than the values usually obtained). According to these studies, it appears that the different macromolecular chain architectures have a direct influence on the macroscopic behavior of the films. Indeed, it is well known today that the emulsion polymerization process is very efficient for controlling the structure of latex particles and of the corresponding films. By introducing monomers (feed rate and composition), it is possible to synthesize a broad range of copolymer structures (from statistical to tapered). The macromolecules are more or less homogeneously distributed within the polymer particles.<sup>6–10</sup> This idea was already applied to PSAs to elaborate "core-shell"-like particles in which the core is quite cohesive and the shell is adhe-

Correspondance to: E. Papon (papon@enscpb.fr).

sive.<sup>11,12</sup> Because both hard and soft phases are generally incompatible, it is often necessary to improve the "adhesion" at the core-shell interface; the most common ways to achieve this are to develop chemical bonds<sup>13</sup> or to build interpenetrating networks (IPNs).<sup>14</sup> With improved adhesion at the core-shell interface, phase separation is avoided and the particle structure is preserved in the coalesced films.

In this study, we synthesized methyl methacrylate (MMA) and 2-ethyl hexyl acrylate (EHA) copolymers by free-radical emulsion polymerization and studied the correlations between the structure [on the nanoscopic (macromolecules) and mesoscopic (polymer particles) scales] and the tack properties (on the macroscopic scale) of the PSA films. The MMA-EHA comonomer system was chosen because of its special features, which include incompatibility with each of the corresponding homopolymers (PMMA and PEHA), insolubility of PMMA in EHA, and much higher reactivity of MMA radicals than EHA radicals (measured in homogeneous solution polymerization). These features ensure a good compromise between cohesion (given by MMA units) and instantaneous adhesion (given by EHA units). Our study<sup>15</sup> using the Batch process proved that the structure of the polymer particles obtained had MMA-rich cores coated by increasingly rich concentric outer layers of EHA, indicating a kinetic rather than a thermodynamic control. To relate macroscopic characteristics to the particle structures, PSA films were obtained by latex coalescence, and their tack properties were evaluated with a Mechano-Optical Tack-Tester<sup>16</sup> (MOTT; from Atofina's GRL Department). The films typically had the same mesoscopic heterogeneity as the polymer particles, and optimal tack resulted from copolymers with MMA-EHA units in the narrow composition range of 35/65 to 25/75 (molar ratios). To extend this range, a semicontinuous (SC) process (i.e., continuous addition of monomer mixtures into the reactor at controlled feed rates and compositions) is required. The main advantage of the SC mode versus the Batch process is the constant low level of the monomer concentration in the polymer particles, which allows regular growing of the polymer particles. Moreover, if starved conditions are imposed (i.e., feed rate lower than polymerization rate), the copolymerization occurs exclusively between particles, allowing the instantaneous particle composition to be almost equivalent to that of the feed.

In this study, constant feed rates with various comonomer blends ("SC Mixture") and separate, inversely varying feedings with both monomers ("SC Gradient") were used. Both processes ensure global homogeneity in the polymer particles because the SC Mixture process is expected to give a composition drift near 0%, whereas the SC Gradient process is expected to produce particles composed of successive layers

whose composition gradually varies from the "hard" (MMA-rich) to the "soft" (EHA-rich) phase so that each layer would automatically be compatible with its surrounding layers. The effect of the composition profile has already been explored by Asua et al.<sup>5</sup> for the same monomers, but the composition drift was limited to  $\pm 10\%$  for a global molar ratio of 15/85 for MMA-EHA units. In our experiments, we used a broad global composition molar ratio range for MMA-EHA units of 60/40 to 0/100, with a composition drift range of 0 to 100% around the particles.

The first focus of this article is the determination of the kinetics and the exact characterization of the final particle composition and structure produced during the course of SC Mixture and SC Gradient processes and comparison of the results with those from the Batch process.<sup>15</sup> Next, characterization by tack measurements of the PSA films obtained from the various latexes is presented and discussed. Finally, correlations between polymer structure and characteristics of PSA films are proposed.

## EXPERIMENTAL

### Chemicals

MMA (99% purity, stabilized by 10–100 ppm methyl hydroquinone) and EHA (98% purity, stabilized by 10 ppm methyl hydroquinone), purchased from Aldrich, were distilled before use and stored at 0–5°C. Initiator (potassium persulfate, KPS), emulsifier (sodium dodecyl sulfate, SDS), and buffer (disodic phosphate,  $\text{Na}_2\text{HPO}_4$ ) were purchased from Merck and used without further purification.

### Elaboration of adhesive material

#### Process

The syntheses were carried out in a 250-mL glass reactor equipped with a mechanical stirrer, a flux condenser, a nitrogen inlet, and a septum through which samples for kinetic studies were taken. Reaction mixtures were heated at 80°C and stirred at 400 rpm under nitrogen flow. In a typical experiment, a mixture of 100 mL of distilled water, 0.06 g of  $\text{Na}_2\text{HPO}_4$ , and 0.2 g of SDS was stirred and heated at 80°C for  $\sim 10$  min. Then, a solution of 0.1 g of KPS in 20 mL of distilled water was added and the copolymerization was conducted. Copolymerization was accomplished by adding 20 mL of the comonomer system into the reactor in one step for the Batch process and with syringes monitored by insulin pumps (Perfusor<sup>®</sup> Compact from B. Braun Medical) for the SC processes. A constant feed rate of each comonomer blend (MMA-EHA molar composition ranging from 60/40 to 0/100) was used for the SC Mixture mode. In the SC Gradient mode, the separate monomer supplies were

TABLE I  
Feeding Schedule for the SC Gradient Polymerization of 50/50 MMA-EHA Systems

Time range (min)	$r_{\text{MMA}}$ (mL/h)	$r_{\text{EHA}}$ (mL/h)	% MMA (mol ratio)	$n_{\text{MMA}}$ (mmol)	$n_{\text{EHA}}$ (mmol)
0-10	6.8	0.0	100	10.7	0.0
10-20	6.2	1.2	91	9.7	1.0
20-30	5.5	2.4	82	8.7	1.9
30-40	4.9	3.6	73	7.7	2.9
40-50	4.3	4.8	64	6.8	3.9
50-60	3.7	6.0	55	5.8	4.8
60-70	3.1	7.2	45	4.8	5.8
70-80	2.5	8.4	36	3.9	6.8
80-90	1.8	9.7	27	2.9	7.7
90-100	1.2	10.9	18	1.9	8.7
100-110	0.6	12.1	9	1.0	9.7
110-120	0.0	13.3	0	0.0	10.7

controlled in such a way that the MMA-EHA molar ratio varied from 100/0 to 0/100 during the feeding time (for each overall composition), as shown in Table I for 50/50 MMA-EHA overall composition. The feed rates were chosen to ensure the establishment of starved conditions (i.e., instantaneous composition of the synthesized chains equivalent to that of the added monomer mixture).

#### Kinetic study

Aliquot samples were taken from the reaction mixture at different polymerization times and poured into aluminum foil dishes. The polymers were precipitated by methanol in the presence of small amounts of hydroquinone (to prevent any further polymerization). The copolymers were dried to constant weight under reduced pressure in an oven at 60°C. The overall conversion equals the ratio between the weight of polymer in the reactor and the total amount of monomer added. The instantaneous monomer conversion equals the ratio between the weight of polymer in the reactor and the total amount of monomer that was already added.

#### Composition of the copolymers

The compositions of the copolymer samples were determined by proton nuclear magnetic resonance spectroscopy ( $^1\text{H-NMR}$ ; in  $\text{CDCl}_3$ , using an AC 250 MHz Bruker spectrometer) by integration of the characteristic signals of EHA and MMA units at 3.90 and 3.60 ppm, respectively.

#### Particle size evaluation

The mean particle diameter of latexes was evaluated by LASER granulometry (wavelength  $\lambda = 633 \text{ nm}$ ) with the Malvern Instruments Zetasizer 3000HS apparatus.

#### Characterization of PSA films

##### PSA samples

Films (200  $\mu\text{m}$  thickness) were prepared by coating aluminum sheets with the final latexes (at 100% conversion), drying in an oven under reduced pressure, and cutting of rectangular 20  $\times$  30-mm pieces.

##### Differential scanning calorimetry

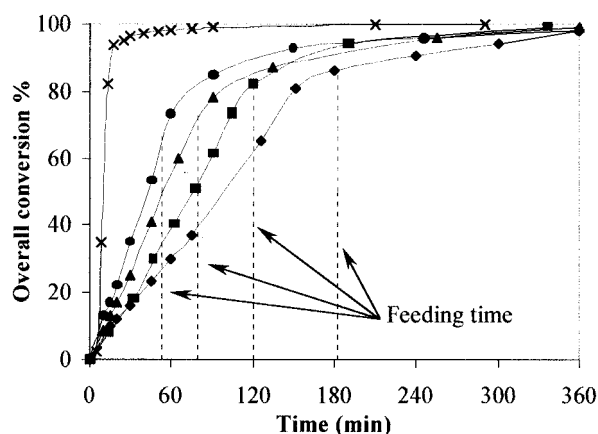
The glass transition temperatures ( $T_g$ ) of the materials were determined with a Mettler Toledo DSC 30 system (equipped with a low temperature cell and TC10/TC15 units). Samples (30–40 mg) were scanned from  $-100$  to  $160^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

##### Tack measurement with the MOTT

Tack measurements were achieved at controlled temperature, using the MOTT. As previously described,<sup>16</sup> the tack strength ( $F_{\text{tack}}$ ) is the maximum force ( $F$ ) measured during the pulling up of a quartz probe, after contact with the adhesive film for a determined contact time ( $t_c = 5 \text{ s}$ ), under a controlled contact stress ( $P_c = 1 \text{ MPa}$ ). The tack stress ( $\sigma_{\text{tack}}$ , MPa) is determined by  $\sigma_{\text{tack}} = F_{\text{tack}}/A$ , where  $A$  is the actually wet probe area. The film strain ( $\varepsilon$ ; thickness variation during the separation step) is determined by  $\varepsilon = r \times t$ . The tack energy  $G_{\text{tack}}$  ( $\text{J}/\text{m}^2$ ) is given by:

$$G_{\text{tack}} = \frac{r}{A} \int_i^j F(t) dt \quad (1)$$

where  $r$  is the pulling controlled rate ( $r = 0.5 \text{ mm}/\text{s}$ ).

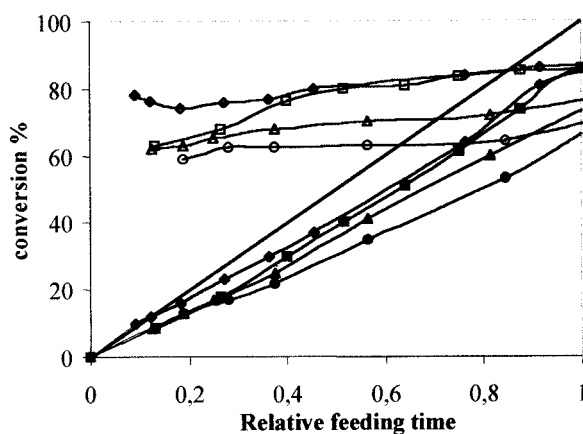


**Figure 1** SC Mixture polymerizations: overall conversion of MMA-EHA 50/50 blends at different feed rates (◆, 6.6 mL/h; ■, 10 mL/h; ▲, 15 mL/h; ●, 22.5 mL/h) with reference to Batch copolymerization (X).

## RESULTS AND DISCUSSION

### Kinetic studies

To control the distribution of MMA and EHA units in the polymer chains as well as in the polymer particles, it is first necessary to establish the starved feed conditions. To establish these conditions, the kinetics of the SC Mixture polymerizations for 50/50 MMA-EHA blends were studied according to various feed rates. The variations of the overall conversion versus time data for the SC Mixture polymerizations are compared with those of the Batch copolymerization performed under similar conditions in Figure 1. The polymerization rate seems to strongly depend on the feed rate. It is also possible to compare the evolution of the instantaneous conversions versus relative feeding time (i.e., the ratio between the reaction time and the total feeding time) for each feed rate (Figure 2). The results indicate that the instantaneous conversion increases when the feed rate decreases; therefore, the lower the feed rate, the more established are the starved conditions (and the lower the instantaneous concentration of monomer in polymer particles). On the other hand, quite constant polymerization rates are observed from ~10% conversion, which indicates that the progressive feeding does not prevent steady polymerization. The size and number of particles per volume unit were simultaneously evaluated. The example reported in Figure 3 for a 10 mL/h feed rate confirms that the nucleation of polymer particles is completed after ~10% conversion. After 10% conversion, the number of particles does not vary when their size increases with conversion, which is in accordance with fairly monitored polymerization processes. These results indicate that at low feed rates ( $\leq 10$  mL/h), the feeding conditions are close to starved conditions. These rates were therefore applied to the SC Gradient process to

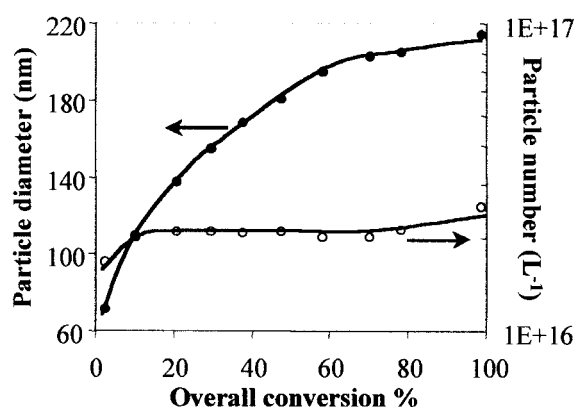


**Figure 2** SC Mixture polymerizations of MMA-EHA 50/50 blends at different feed rates: overall conversion at feed rates of 6.6 (◆), 10 (■), 15 (▲), and 22.5 (●) mL/h; and instantaneous conversion for 6.6 (◇), 10 (□), 15 (△), and 22.5 (○) mL/h. The diagonal represents the ideal starved conditions (when the feed rate is lower than or equals that of polymerization).

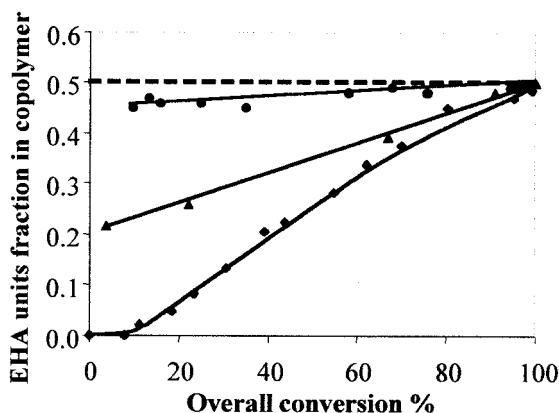
impose a total molar feed rate equivalent to that of the 10 mL/h SC Mixture (i.e.,  $6.4 \cdot 10^{-2}$  mol/h). The next question is how to determine the distribution of MMA-EHA units along the macromolecular chains and around the polymer particles.

### Copolymer architecture

To complete the kinetics study,  $^1\text{H-NMR}$  analyses were performed during the course of SC Mixture, SC Gradient, and Batch copolymerizations for a global 50/50 MMA-EHA molar composition. The evolutions of the cumulative copolymer compositions are reported in Figure 4. As expected, SC processes allow the monitoring of the cumulative copolymer composition, the value of which remains close to that of the feeding. This value is roughly constant (~50/50 MMA-EHA units) for SC Mixture processes at 10

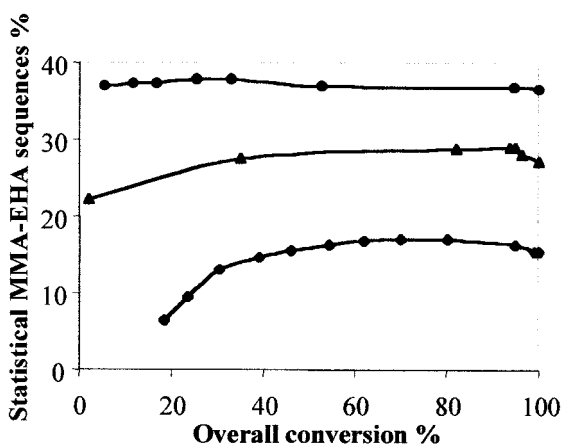


**Figure 3** Particle diameter (●, nm) and particle number (○,  $\text{L}^{-1}$ ) versus overall conversion for a 50/50 MMA-EHA SC Mixture polymerization at 10 mL/h feed rate.

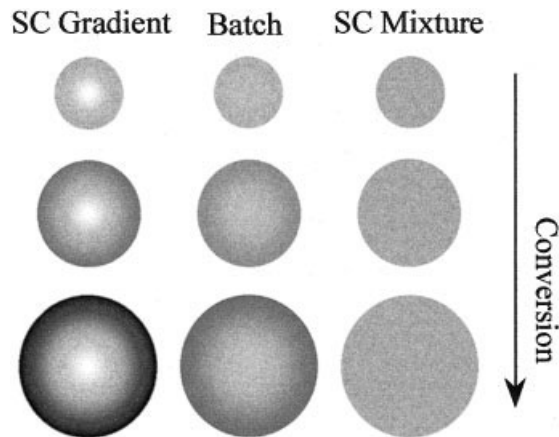


**Figure 4** Cumulative copolymer composition (in molar fraction of EHA units) versus overall conversion for SC Gradient (◆), Batch (▲), and SC Mixture (●) processes (10 mL/h).

mL/h, and regularly varying (from 100/0 to ~50/50 MMA–EHA units) for SC Gradient processes. For Batch processes, it has been previously explained that the progressive incorporation of EHA units into the copolymer is in good agreement with both the water solubility of MMA and EHA monomers and the relative reactivity of their corresponding free radicals.<sup>15</sup> Comparison of the evolution of the cumulative amount of MMA–EHA copolymer sequences (Figure 5) with that of MMA–MMA homopolymer sequences (as inferred from a splitting of the <sup>1</sup>H-NMR characteristics peaks at  $\delta = 3.6$  ppm) gives additional information. Primarily, homogeneous statistical copolymerization occurs in the SC Mixture process. In contrast, the (co)polymer chains obtained by Batch or SC Gradient processes are more heterogeneous and, thus, contain fewer statistical sequences. In these latter cases, the number of statistical sequences increases



**Figure 5** MMA–EHA copolymer sequences versus overall conversion for SC Gradient (◆), Batch (▲), and SC Mixture (●) processes (10 mL/h).



**Figure 6** Assumed polymer particles structures induced by SC Gradient, Batch, and SC Mixture polymerizations of 50/50 MMA–EHA systems: (dark shading) PEHA, (light shading) Copolymer, (no shading) PMMA.

with conversion up to a plateau. The final value reached at the plateau decreases when the composition heterogeneity of the chains increases.

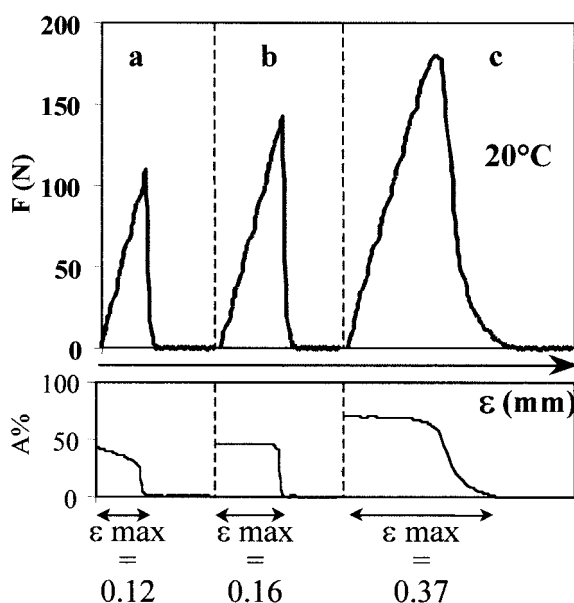
### Structure of the latex particles

The polymerization process dictates the particle composition, so management of the particle structure must be considered. As shown in Figure 6, homogeneous structures can be assumed to result from the SC Mixture process, and submicron-scale heterogeneous structures can be assumed to result from Batch and SC Gradient processes. In the case of SC Gradient polymerizations, one might think that the hydrophilic MMA-rich chains, which are synthesized in the early stage of the process, could migrate towards the particle–water interface. However, throughout the reaction, the viscosity of the polymer particles remains very high. Indeed, when starved conditions are established, the monomer concentration in particles remains very low. Furthermore, because of the emulsion polymerization mechanisms, each macromolecule reaches a very high molar mass ( $\sim 10^6$  g/mol). Moreover, the chains synthesized first are comprised of a great percentage of MMA units (100% at 10% conversion and 90% at 25% conversion, as shown in Figure 4). These macromolecules are not easily swelled by EHA monomer, have high  $T_g$  values (higher or equals to the reaction temperature), and, at the same time, have high molar masses. For these thermodynamic reasons, there is only a weak probability that MMA-rich chains diffuse towards the particle surface and that an upset of the initial particle structure takes place. Finally, the results of the kinetics study, supplemented by the evolution of the size and number of particles with conversion, prove that no nucleation occurs after 10% conversion. Therefore, it can be concluded that for conversions

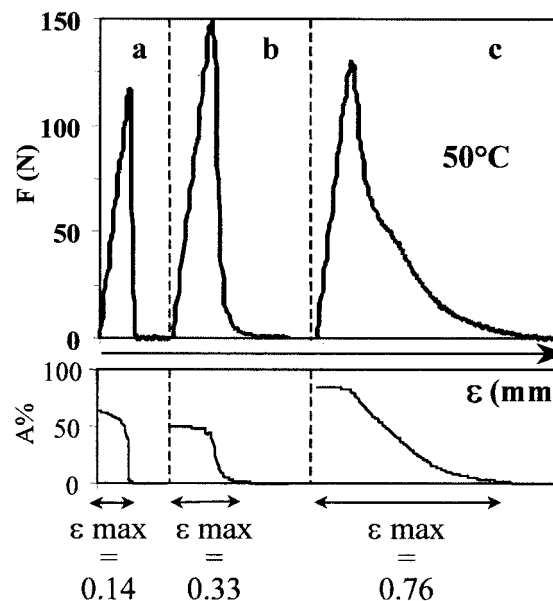
>10%, the copolymer composition is equivalent to that of the feed. For all these reasons, we assume that the final particle structure is controlled by a kinetic rather than a thermodynamic factor and that the particle structure has a MMA-rich core that is surrounded by chains with progressively increasing EHA content, with an outer shell that is composed of nearly pure PEHA (as presented in Figure 6). On the other hand, the particles synthesized by a Batch process adopt an intermediate structure, which is more homogeneous than that of SC Gradient particles but more heterogeneous than that of SC Mixture particles, because of the MMA–EHA chemical characteristics.

To confirm the proposed structures, DSC analyses were conducted to evaluate the  $T_g$  values of films resulting from SC Mixture polymerizations. The  $T_g$  values are about  $-10^\circ\text{C}$ , which is in agreement with the homogeneous structure and composition of the film. Films resulting from Batch and Gradient processes have very broad transition fields (sets of microdomains with varying compositions, ranging from MMA-rich to EHA-rich) that may account for their heterogeneous structures.

In conclusion, the instantaneous composition of polymer particles is close to that of the feed at every moment, and the polymerization process can control the structure of the polymer particles. Homogeneous particles result from SC Mixture polymerizations and heterogeneous particles (MMA-rich in the core, increasing EHA richness in the shell) result from SC Gradient polymerizations.



**Figure 7** Tack curves at  $20^\circ\text{C}$ : strength [ $F$  (N)] and contact area percent ( $A\%$ ) versus strain [ $\varepsilon$  (mm)] for (a) SC Gradient, (b) Batch, and (c) SC Mixture films ( $t_c = 5$  s,  $P_c = 1$  MPa).

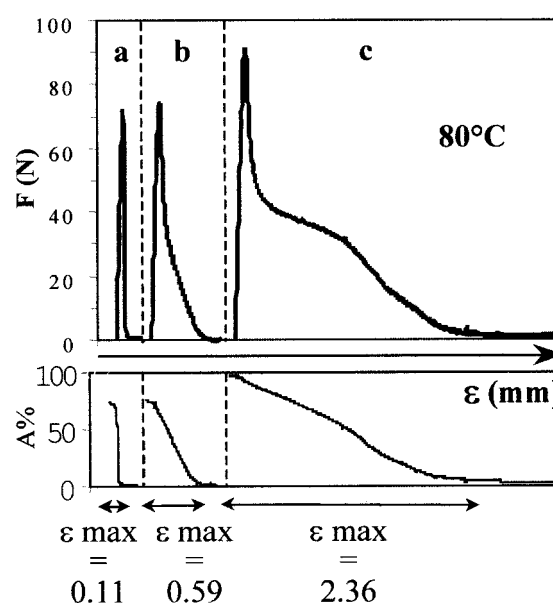


**Figure 8** Tack curves at  $50^\circ\text{C}$ : strength [ $F$  (N)] and contact area percent ( $A\%$ ) versus strain [ $\varepsilon$  (mm)] for (a) SC Gradient, (b) Batch, and (c) SC Mixture films ( $t_c = 5$  s,  $P_c = 1$  MPa).

#### Tack properties of the PSA films resulting from the various latexes

##### Influence of the process

To compare the behaviors of films resulting from the various polymerization processes, tack parameters were measured for 50/50 MMA–EHA SC Mixture, SC Gradient, and Batch samples. The variations of both the force ( $F$ ) and the wet area ( $A\%$ ) versus the film strain ( $\varepsilon$ ) during the pulling step of tack measure-



**Figure 9** Tack curves at  $80^\circ\text{C}$ : strength [ $F$  (N)] and contact area percent ( $A\%$ ) versus strain [ $\varepsilon$  (mm)] for (a) SC Gradient, (b) Batch, and (c) SC Mixture films ( $t_c = 5$  s,  $P_c = 1$  MPa).

TABLE II  
Tack Parameters of 50/50 MMA-EHA SC Gradient, Batch, and SC Mixture Films at Various Temperatures

T (°C)	SC Gradient				Batch				SC Mixture			
	$\sigma_{\text{tack}}$ (MPa)	$G_{\text{tack}}$ (J/m <sup>2</sup> )	A (%)	$\varepsilon_{\text{max}}$ (mm)	$\sigma_{\text{tack}}$ (MPa)	$G_{\text{tack}}$ (J/m <sup>2</sup> )	A (%)	$\varepsilon_{\text{max}}$ (mm)	$\sigma_{\text{tack}}$ (MPa)	$G_{\text{tack}}$ (J/m <sup>2</sup> )	A (%)	$\varepsilon_{\text{max}}$ (mm)
20	1.45	87	54	0.13	2.3	180	43	0.16	1.83	250	76	0.37
50	1.18	81	67	0.14	1.56	160	56	0.18	1.08	220	84	0.74
80	0.67	52	90	0.12	0.71	87	79	0.30	0.70	480	96	2.4

ments at 20, 50, and 80°C are shown in Figures 7, 8, and 9, respectively. The characteristic tack parameters of the films at 20, 50, and 80°C are summarized in Table II.

Quite different behaviors are observed. At 20°C, SC Mixture films have reasonable tack properties; that is, acceptable wetting of the probe during the contacting step and suitable tack force and tack energy during the pulling step. At the same temperature, both Batch and SC Gradient films are too cohesive (limited wet area and sharp adhesive failure) to behave as suitable PSA materials. With increasing temperature, the tack properties of the SC Mixture films improve (quite good capacities for wetting and deformation and stress dissipation due to formation of fibrils at 50°C) and then collapse (lack of cohesion at 80°C), resulting in cohesive failures. The tack properties of Batch films get somewhat better at 50 and even at 80°C, but they always remain at a low level. The poor PSA abilities of SC Gradient films are not affected by temperature, but odd behaviors are observed; for example, considerable elastic solid behavior at the bonding step (poor wetting), together with considerable viscous liquid behavior at the separation step (low energy cohesive failures).

All of these results can be correlated with the structures of the films. The nearly homogeneous SC Mixture films are likely to be composed of long, flexible, and strongly entangled polymer chains. Therefore, suitable wetting of the MOTT sensor can be achieved during the bonding step when dissipation of energy in the bulk of the film (up to fibrillation) is favored during the separation step. With increasing temperature, chain disentanglement becomes easier and easier, and there is an increase in the wetting ability with the further loss of cohesion. The submicron-scale heterogeneity of SC Gradient films, with hard PMMA-rich microdomains dispersed in a soft EHA-rich matrix, can account for both their elastic response to compressive stress (bonding step) and their viscous response to pulling stress (separation step). The disconnection between adhesive and cohesive properties, due to a lack of compatibility between the hard and soft domains, can account for the inconsistent behavior of SC Gradient films. In the case of Batch films, compatibility between the MMA-enriched microdo-

main and the EHA-enriched matrix is more likely because of the presence of tapered-type copolymers (i.e., polymer chains whose constitution changes progressively from PMMA sequences at one end to PEHA sequences at the other end). As a consequence, adhesion and cohesion balance enough to allow the development of modest tack properties.

#### Influence of the overall film composition

In a previous work,<sup>15</sup> the influence of the overall film composition on the PSA behavior of Batch films was demonstrated. Tack properties are achieved with MMA/EHA compositions ranging from 50/50 to 25/75. In this range, there is an evolution from rather elastic behavior (high  $F_{\text{tack}}$ , low  $A\%$ , low  $G_{\text{tack}}$ ) to rather viscoelastic behavior (low  $F_{\text{tack}}$ , high  $A\%$ , high  $G_{\text{tack}}$ , associated with fibrillation phenomena that account for high film deformation and energy dissipation). Below the critical 25/75 composition, cohesive failures occur at the end of the separation step and the films no longer show tack properties, only pegosity (instantaneous adhesion without any cohesion).

In this work, PSA films were prepared from SC Mixture and SC Gradient polymerizations of 40/60–20/80, 50/50, and 0/100 MMA-EHA systems (at >50% MMA units, the cohesion of the films is so high that instantaneous adhesive properties do not exist). As a general trend (Figure 10), cohesive behaviors (high  $F_{\text{tack}}$ , low  $G_{\text{tack}}$ , adhesive failures) are observed at high fractions of MMA units (i.e., at low  $F_{\text{EHA}}$ :EHA units fractions), whereas adhesive behaviors (low  $F_{\text{tack}}$ , high  $G_{\text{tack}}$ , fibrillation phenomena, cohesive fail-

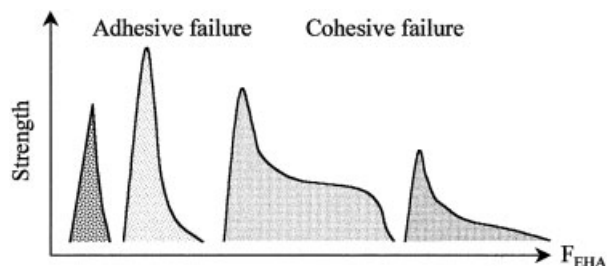
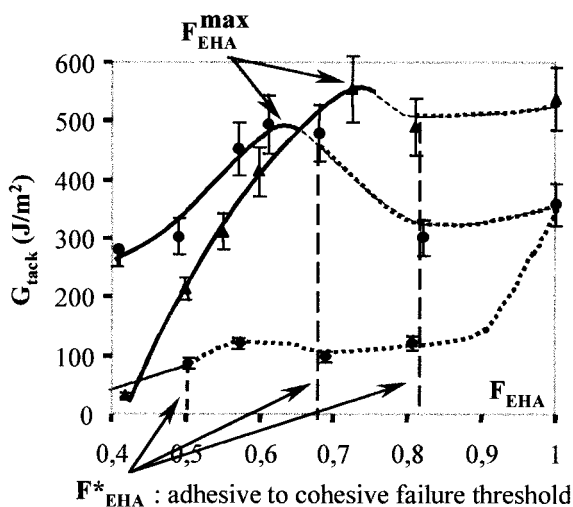


Figure 10 Evolution of the tack curves with  $F_{\text{EHA}}$  in the PSA films.



**Figure 11** Tack energy versus  $F_{EHA}$  for (◆) SC Gradient, (▲) Batch, and (●) SC Mixture films.

ures) are observed at high  $F_{EHA}$ . However, fibrillation is never observed in the case of SC Gradient films. The variations of  $G_{tack}$  with  $F_{EHA}$  at 20°C (Figure 11) point out the unsuitability of SC Gradient films for use as PSAs. On increasing  $F_{EHA}$ , compatibility between the MMA-rich microdomains and the soft matrix is achieved less and less, which explains why only cohesive failures are observed at the separation step. The value of  $G_{tack}$  for SC Mixture and Batch films increases to a maximum ( $F_{EHA}^{max}$ ), corresponding to the best compromise between bulk cohesion and instantaneous outer surface adhesion. The value of  $F_{EHA}^{max}$  is lower for SC Mixture than for Batch films (~0.6 versus 0.7), which is in accordance with the absence of MMA-rich hard microdomains that are able to improve the cohesive behavior at the separation step. Soon after the maximum value is reached, the transition from adhesive failure to cohesive failure occurs at  $F_{EHA}^*$  (0.7 and 0.8 for SC Mixture films and Batch films respectively). Thus, even if SC Mixture polymerization can give new direct access to MMA-EHA PSA materials, the composition range is limited between 50/50 and 20/80 MMA-EHA monomer units. Too many MMA units induce poor instantaneous adhesion, whereas too many EHA units deprive the films of enough cohesion.

## CONCLUSION

This study confirms the possibility of adjusting the tack properties of PSA by direct synthesis rather than by formulation. The synthesis is based on free-radical emulsion polymerization of two complementary monomers (MMA and EHA). Control of the composition of the latex particles, the structure of the corresponding films, and of their tack properties can be achieved by the method of introduction of the mono-

mers. Homogeneous structures, such as those obtained from the SC Mixture mode, can lead to adequate PSA behavior, provided suitable chain lengths and entanglements are ensured. Some degree of heterogeneity, as obtained from the Batch mode, is opportune as long as the hard microdomains dispersed in the soft matrix are made compatible by, for instance, tapered or even graft-type copolymers. On the contrary, too much homogeneity as well as too much phase segregation does not result in good PSA behavior because the films are either too sticky or not sticky enough. The tack properties depend on temperature. The PSA films are less cohesive with increasing temperature and less adhesive with decreasing temperature. These properties also depend on the composition of the copolymers in that a limited composition range, with one characteristic optimum, is found for each type of suitable structure. For example, interesting possibilities are likely to occur in such fields as "multistick and release" PSA (30/70 Batch), "long-lasting" PSA (30/70 SC Mixture), or even "Hot-Melts" (50/50 Batch).

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