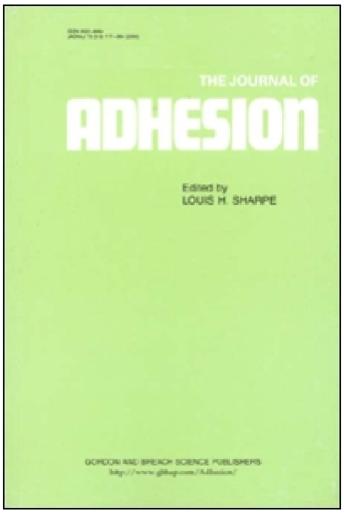

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Styrene-Butadiene Polytelomers for Pressure-Sensitive Applications*

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Novel styrene-butadiene polymer latex compositions and their utility for pressure-sensitive and other adhesive applications are described. These compositions, termed polytelomers, are based on the concept of synthesising sequentially a low glass transition temperature, high molecular weight (polymeric) fraction, followed by a high glass transition, low molecular weight (telomeric) fraction, in an attempt to simulate the compounding of elastomeric adhesives. Some of the described compositions can exhibit multiphase morphology, having discrete styrene-rich domains surrounded by butadiene rich phase, both of these phases being embedded in a "honeycomb" carboxyl-rich phase. The compositions were characterized by dynamic mechanical spectroscopy and by electron transmission microscopy, as well as by molecular weight distribution and glass transition temperature range data. Examples of adhesive applications are also given.

Keywords: Pressure-sensitive adhesives; styrene-butadiene latex; two-stage synthesis; polytelomers; film morphology; dynamic mechanical analysis; peel strength

1. INTRODUCTION

In the last 20 years or so, the sucessful commercialization of phase-separated styrene-diene-styrene thermoplastic elastomers has stimulated extensive investigations of two-stage and three-stage emulsion polymerization processes, in order to obtain polymeric particles having phase-separated morphologies. These emulsion polymerization

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approaches usually involve a sequential polymerization of a hard phase and a soft phase within a single polymer particle in a batch or a continuous monomers feed process. In this way a variety of final single-particle morphologies of the polymer particles can be obtained [1–4]. Often these polymerization processes are termed "core-shell", though other morphologies (*e.g.* "strawberry") are sometimes observed. The various factors in synthesis (*e.g.* the ratio of the soft and hard phases, their surface free energies, the effects of cross-linkers), which determine the degree of phase separation during synthesis and, thereby, the final particle morphology, have been recently reviewed [5]. The term latex interpenetrating networks (LPN) has also been used in this context, particularly when crosslinking monomers are used in an attempt to prevent gross phase separation [6]. Generally, these investigations deal with polymers in the high molecular weight range, which, in addition, may be cross-linked.

We have adapted the basic idea of the soft/hard "core-shell" process to obtain compositions suitable for elastomeric adhesives applications, *e.g.* pressure-sensitive, laminating, or contact adhesives [7, 8]. These adhesives are usually compounded from soft, high molecular weight polymers and hard, low molecular weight resins. Accordingly, we have designed two-stage processes, in which the first stage yields a low T_g polymer and the second stage yields a high T_g low molecular weight "polymer", using styrene and butadiene as the main monomers. In order to obtain the desired very low molecular weight resins, we have used a large amount of chain transfer agent in the "hard" stage of the reaction. Since such a process is technically known as telomerization [9], (the chain transfer reaction being the predominant molecular weight determining mechanism), we use the term polytelomerization and polytelomers for the overall two-stage process and the materials so obtained.

Our investigations focused on pressure-sensitive applications, in which the polymer and resin are normally compatible or just about phase-separated [10, 11]. We have not, therefore, endeavored to obtain any specific particle morphologies, though some of the polytelomeric adhesive films obtained had a two-phase or a three-phase colloidal microstructure.

2. EXPERIMENTAL

2.1. Synthesis

Carboxylated styrene butadiene latexes were prepared by the usual continuous monomer addition emulsion polymerization process, using a 30 nm particle size polystyrene seed latex to control the particle size, and hence the rate of polymerization. The monomeric composition for each polymerization stage was fed into the reaction mixture sequentially without normally letting the first stage react to substantially complete conversion. The latexes obtained had particle sizes of around 165 nm and solids content of about 50% at essentially 100% conversion. The latices were stabilized by about 2.0% of copolymerized itaconic acid, which was proportionally split between the polymeric and telomeric stages. They were stripped by steam distillation with a chemical stripping package, after neutralization with concentrated ammonia to pH 7.0–7.5. The free styrene content of the stripped latexes was typically less than 0.05%.

2.2. Characterizations

Glass Transition Range Temperature (T_g) The T_g was obtained with a DuPont DS10 differential scanning calorimeter as a midpoint determination at 10°C/min heating rate. Generally, the T_g transitions were broader for the polytelomers than for the single stage polymers.

Molecular Weight. The Gel The gel content was determined gravimetrically as an insoluble fraction (in toluene, or tetrahydrofuran) of a well-dried polymeric film, using a metal cage of 325 mesh, and allowing the sol to dissolve for 48 hours. *The Sol*: The molecular weight of the sol was determined by GPC using polystyrene of different molecular weights as standards.

Dynamic Mechanical Analysis The mechanical behavior was investigated using a Rheometrics RDA mechanical analyzer in parallel plate geometry. With these measurements the storage modulus G' and the loss modulus G'' were determined. The ratio of G''/G' then gives the damping factor tanδ.

Electron Microscopy Electron transmission micrographs were obtained after the samples of polymer films (both bulk and dry, cryo-ultrathin sections) were stained with osmium tetraoxide to show butadiene-rich regions, or after the samples (dry cryo-ultrathin sections) were stained with a uranyl salt compound to contrast the acid-rich particle surface regions.

3. RESULTS AND DISCUSSION

3.1. Comparison of a Two-Stage Process with a Single Stage Process

3.1.1. Polytelomerization

In Table I the basic composition of a **polymer** 1131 (control) and of the **polytelomer** 1157 is shown, together with the amount of *t*-dodecyl mercaptan (chain transfer agent) to control the molecular weight. Both samples have the same overall composition, the two-stage polytelomer being designed to give a low T_g polymer in the first stage of polymerization, and a high T_g low molecular weight telomer in the second stage of the reaction. The ratio of the first to the second stage was 60/40 on the monomeric weight basis. The first polymeric stage was reacted to about 65% conversion only, when the second stage was started. This is an essential feature of polytelomerization technology, which allows a "mixture" with continuously increasing glass transition and decreasing molecular weight to be synthesized in the second stage.

3.1.2. Characterizations

The change in molecular weight distributions for these two cases, *i.e.* between the polymerization process (polymer 1131) to the polytelomerization process (polytelomer 1157), is remarkable. The polymer has only a slightly broadened molecular weight distribution in the low molecular weight range, whereas the polytelomer has an extremely

TABLE I Comparison of Polymer and Polytelomer properties at Constant overall Composition

	Polymer 1131	*Polytelomer 1157*	
Composition		*"Poly"*	*"Telo"*
Styrene/Butadiene	1.08	0.54	4.0
t-Dodecyl Mercaptan (%)	4.82	0.70	11.0
Molecular Weight Characteristics			
[1]Insoluble (%)	0	2.0	
[2]Insoluble (%)	0	3.4	
[3]M_w (g/mol)	17,000	710,000	
M_w/M_n	2.4	92	
Glass Transition Temperature (°C)			
[4]DSC	-22	-22	
Film Tensile			
[5]Tensile (kg cm^{-2}) /Elogation(%)			
24 hr @	0/0	1/no break	
30 min @ 120°C	0/0	3/2500	

[1] in toluene.
[2] in THF.
[3] weight average of sol portion.
[4] midpoint @ 10°C/min.
[5] 300 mm/min.

broad molecular weight distribution, extending from very low range to very high. These molecular weight distributions are shown in Figure 1. In both cases there is a single T_g of about -22°C, indicating that the polytelomer has not grossly phase-separated. However, electron microscope pictures showed some phase-separated butadiene-poor regions on a scale smaller than the polymer emulsion particle size, Picture 1a. There are also a few randomly distributed regions rich in carboxylation, as shown in Picture 1b. The polymer 1131 has no measurable tensile properties, behaving more like a very heavy oil. The polytelomer is quite weak and its tensile properties are just measurable, the film being extremely tacky.

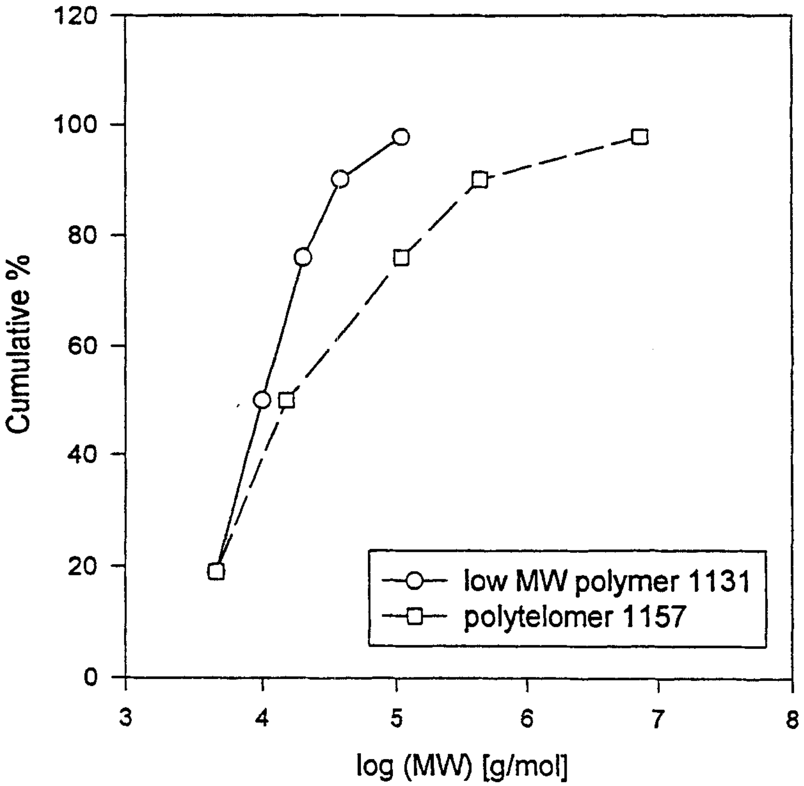
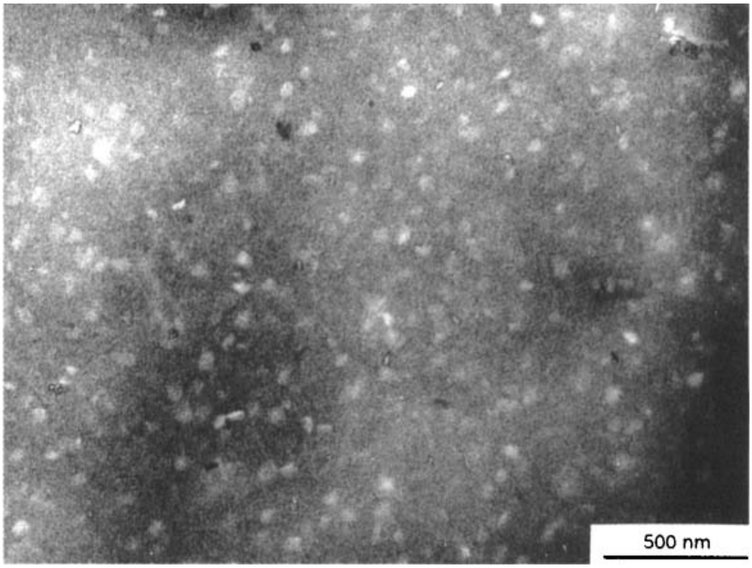
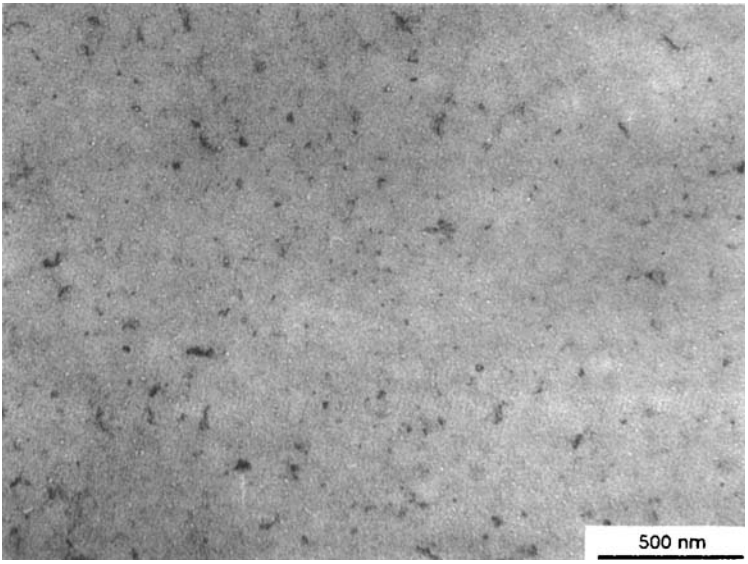


FIGURE 1 Comparison of Molecular Weight Distributions.

The above differences are also reflected in the dynamic mechanical analysis results shown in Figures 2 and 3 for the temperature dependence of G' and tanδ. At 100°C the polytelomer has a G' of about 3 orders of magnitude higher than the polymer; similarly, the tanδ of the polytelomer is about 0.8 in the "rubbery" plateau, whereas the low molecular weight polymer 1131 is so soft that the measurement at high temperatures becomes unreliable, the measured values of tan δ being well in excess of 2. Nevertheless, the mechanical T_g as evidenced by the main peak of tanδ is the same for the polymer and polytelomer. These characteristics suggest that the polytelomer might be a useful pressure-sensitive composition, as discussed further under 3.3.



PICTURE 1a Transmission Electron Micrograph of Polytelomer 1157 Stained with OsO_4.



PICTURE 1b Transmission Electron Micrograph of Polytelomer 1157 Stained with UO_2^{2+} Salt.

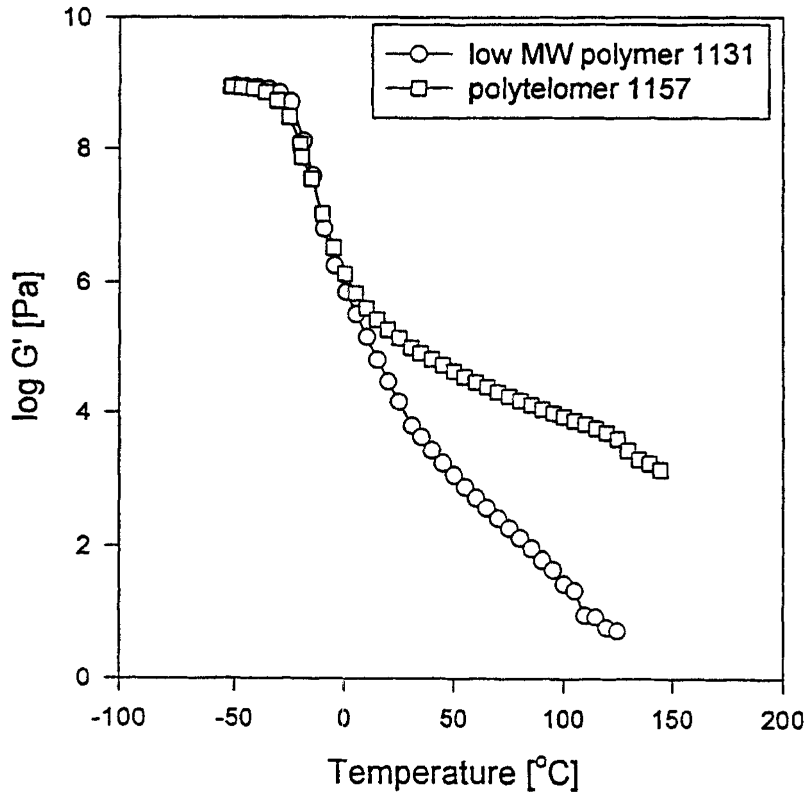


FIGURE 2 Comparison of Temperature Dependence of Storage Moduli G'.

3.2. Some Variations

3.2.1. The Effect of Degree of Conversion of the Polymeric Stage

This important control variable can be exploited to achieve different degrees of cross-linking: the higher the conversion of the polymeric stage, the great degree of cross-linking reactions. This effect is shown in Figures 4 and 5 for a similar composition given in Table I, except that all butadiene in the second stage is replaced with styrene. It is seen that the higher degree of conversion can increase the "rubbery"

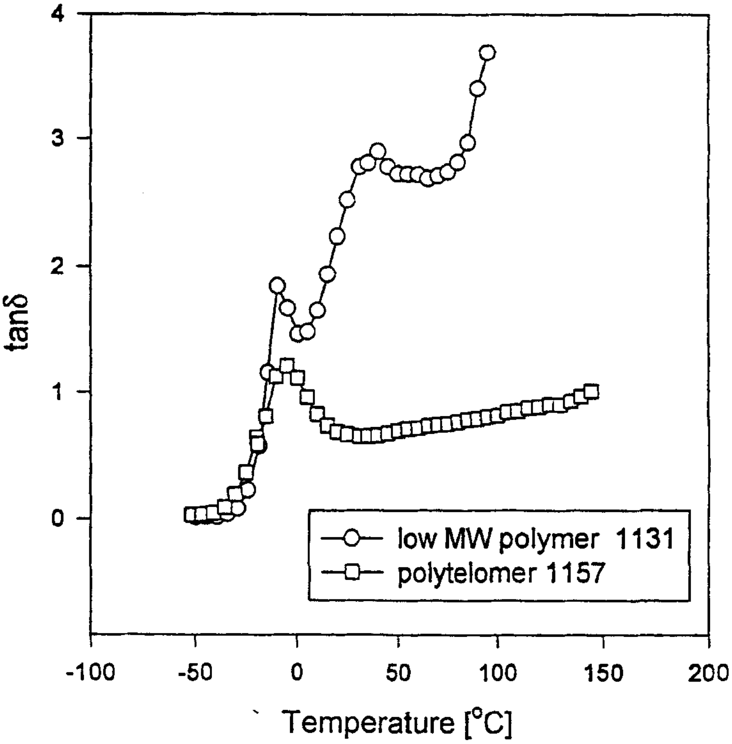


FIGURE 3 Comparison of tanδ.

plateau modulus by about an order of magnitude, and the tanδ begins to decrease quite substantially as compared with the lower conversion case. The glass transition temperature is not affected by these differences in the cross-linking reactions.

3.2.2. The Effect of Molecular Weight of the Telomeric Stage

In Figures 6 and 7 the storage modulus and tanδ are shown for three cases of increasing molecular weight in the telomeric stage (direction toward "core-shell" technology). The dynamic mechanical data show that that the sample with the highest molecular weight has two glass-transitions indicating large-scale phase separation within the polymer

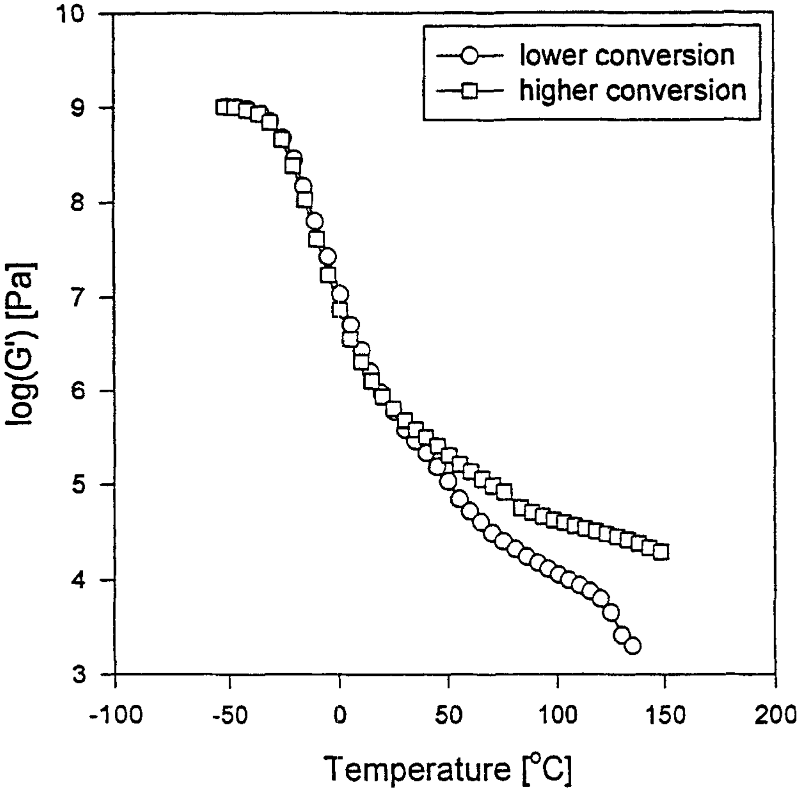


FIGURE 4 Effect of Polymeric Stage Conversion on Storage Moduli *G'*.

particles. As the molecular weight is decreased this two-T_g characteristic disappear and, at the same time, the main T_g is shifted towards higher values, while the modulus becomes lower. This is a classical case of in-process tackification; in other words, as the molecular weight of the telomeric stage is reduced this telomeric composition becomes more compatible with the first stage polymer. The molecular weights were designed for the range of 2000–10000 g/mol.

3.2.3. The Effect of Higher Carboxylation

It is well-known that styrene-butadiene latexes at higher level of carboxylation and also other polymer colloids, develop a particle surface

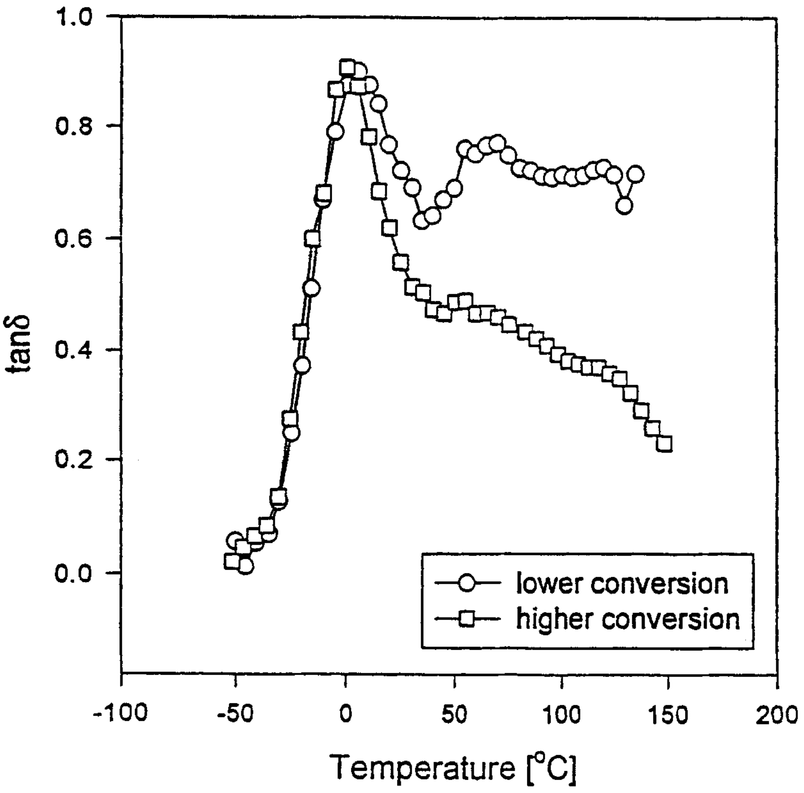


FIGURE 5 Effect of Polymeric Stage Conversion on tanδ.

that contains polymers rich in acidic comonomers. Such colloidal surfaces are, therefore, made of polymer with correspondingly increased glass transition temperature; such surfaces, being extremely thin (about 3–15 nm only), easily deform into a hexagonal pattern during the film-formation process. Such hexagonal patterns, which may persist in the film (depending on the degree of carboxylation) for long periods of time, are the main cause of much improved tensile properties of carboxylated colloid polymers (as compared with non-carboxylated polymer colloids). In Pictures 2a and 2b a sample of a polytelomeric film is shown stained with osmium tetraoxide and a uranyl salt, respectively. It is seen that these films contain styrene-rich

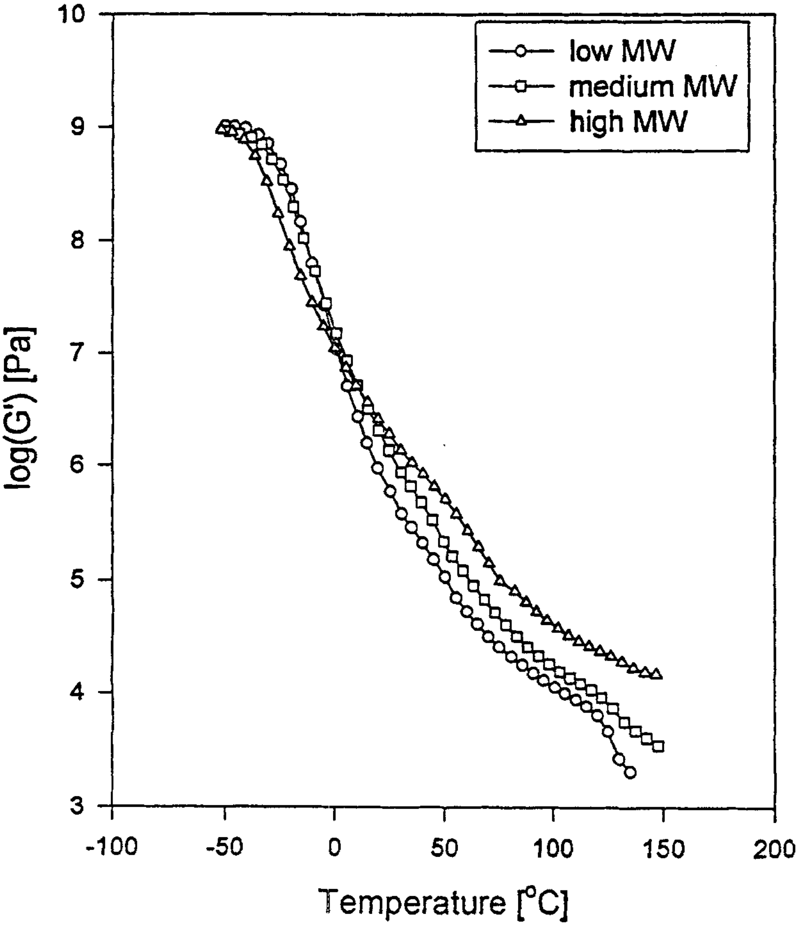


FIGURE 6 Effect of Molecular Weight of Telomeric Stage on G'.

domains as a discontinuous phase (Pic. 2a) and that the butadiene-rich phase appears as the continuous phase. However, the Picture 2b reveals also a hexagonal pattern arising from the surface carboxylation; therefore, the butadiene-rich domains are very likely to be actually discontinuous. Thus, this is an example of a three-phase poly-telomeric film, having (1) discrete low molecular telomeric styrene-rich micro-domains, (2) surrounded by high molecular weight, partially

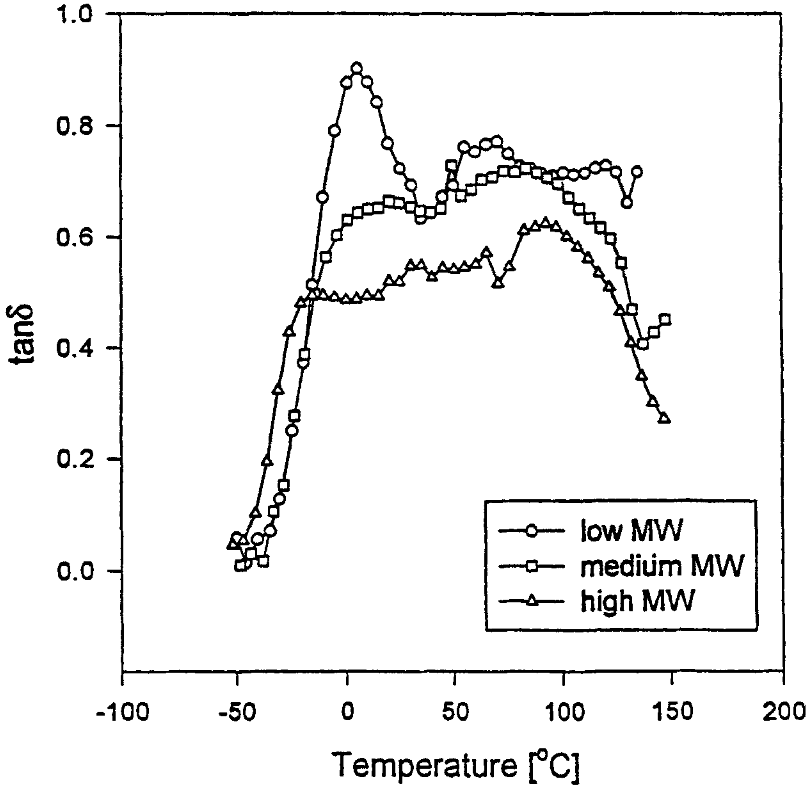
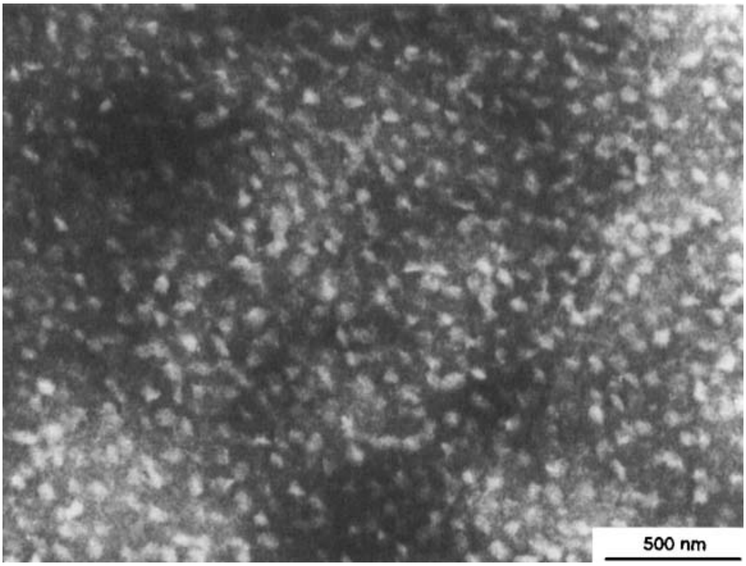


FIGURE 7 Effect of Molecular Weight of Telomeric Stage on tanδ.

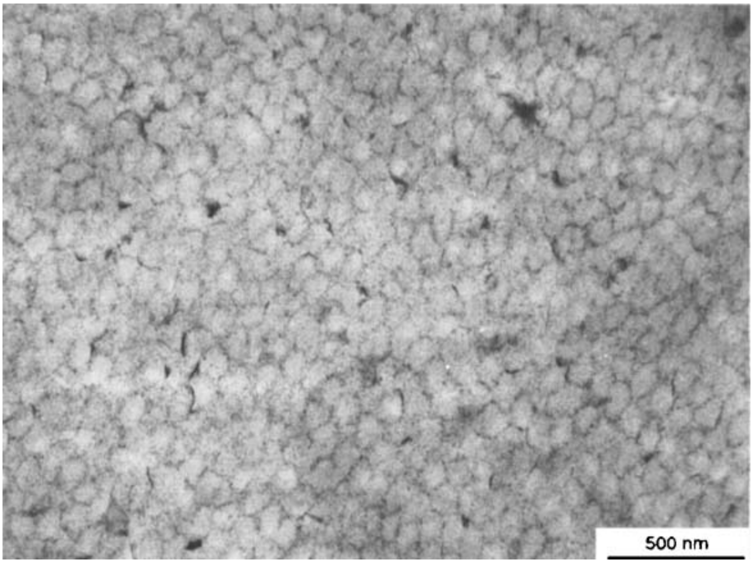
cross-linked, polymeric, butadiene-rich domains, (3) with a highly carboxylated, high T_g hexagonal, "reinforcing", continuous (or interpenetrating?) phase. The carboxylation of these samples was increased by about 3% with methacrylic acid.

3.2.4. The Effect of Higher Glass Transition Temperature of the Polymeric Stage

The above examples dealt with polytelomeric samples having polymeric stages of low glass temperature ranges, corresponding to the styrene/butadiene ratio of 0.25 to 0.75; these polytelomers generally



PICTURE 2a Transmission Electron Micrograph of Highly Carboxylated Polytelomer Stained with OsO_4.



PICTURE 2b Transmission Electron Micrograph of Highly Carboxylated Polytelomer Stained with UO_2^{2+} Salt.

exhibit pressure-sensitive behavior at room temperature. When the styrene/butadiene ratio in the polymeric stage is increased into the 0.75–1.5 range, polytelomers that are non-tacky at room temperature can be obtained. As before, the compositions may exhibit two-phase or three-phase film-forming behavior, depending on the degree of carboxylation, and the molecular weights of the styrene-rich and butadiene-rich regions. It ought to be clear that these compositions, having a low molecular telomeric fraction, may be used for heatsealable or laminating adhesives, as discussed in the next section.

3.3. Adhesive Applications

3.3.1. Pressure-Sensitivity and High Temperature Peel Strengh

In Table II some basic pressure-sensitive and laminating application data are shown for the case of comparing polymers with polytelomers discussed under 3.1. It is seen that the pressure-sensitive properties for the single stage polymers are not useful, whereas the polytelomer sample behaves more or less as a tackified polymer, having a good balance of peel strength, tack and shear. In the laminating application, the polytelomeric sample exhibits improved peel strength at elevated temperatures.

TABLE II Comparison of Polymer and Polytelomer Adhesive Properties

	Polymer 1131	*Polytelomer 1157*
[1]Pressure-Sensitive Properties		
[2]180° Peel Strength (lb/in)	0.6	3.7
Looptack, 30 sec dwell (lb/in)	nil	2.2
Shear, 1" × 0.5" @ 1.0 kg (hr)	nil	4.0
[3]Laminating Propertes		
180° Peel Strength (lb/in)		
@ 23°C	0.9	9.9
@ 70°C	nil	3.2
@ 100°C	nil	1.5

[1] PSTC Standard Methods.

[2] Stainless Steel/Polyester Film.

[3] Coatweight ~ 50 gm^{-2} on polyester film bonded @ 30–35°C to ABS 1/4" thick plastic.

In Figures 8 and 9 the peel strength of a somewhat different polytelomeric sample (no butadiene in the telomeric stage) is shown as a function of the peel rate at room temperature and at 40 °C. The data were obtained as averages of five samples that failed predominantly cohesively (sometimes mixed cohesive/adhesive failure was observed). It can be seen that at the higher temperature (Fig. 9) the peel strength rate dependence is decreasing (as expected); however, at room temperature (Fig. 8) the peel strength "surprisingly" increases at the lowest peel rate. It can be *speculated* that at this low peel rate (or higher temperature), the high T_g styrene-rich telomeric domains begin to deform, and thereby contribute to the peel strength. At the higher peel rates (or lower temperatures) these stiff telomeric microdomains cannot contribute to the peel strength. At 40°C the styrene-rich microdomains became softer, which results in the expected monotonous rate dependence of the peel strength. In a way, the improved, high temperature peel strength is achieved by an analogous mechanism that has been used for balancing the viscosity of engine oils at

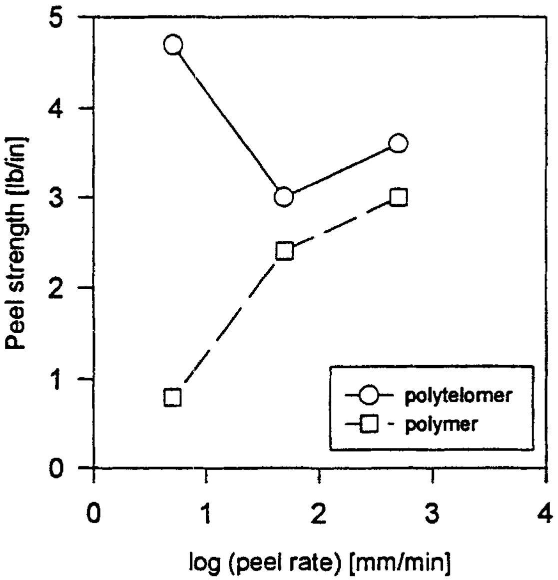


FIGURE 8 Peel Strength at 23°C.

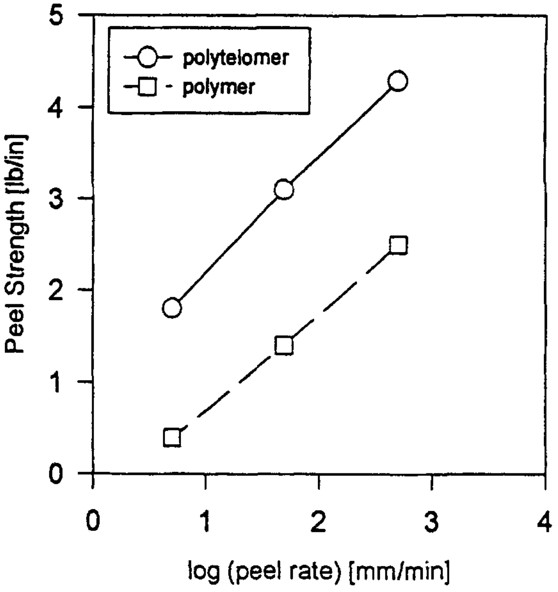


FIGURE 9 Peel Strength at 40°C.

high and low temperatures: in this case the polymeric oil additives are in a coiled conformation at low temperature (suspended) and then they "dissolve" at high temperatures, thereby counteracting the normal decrease of viscosity with temperature.

3.3.2. Heatsealability

In a sense, heatsealability can be perceived as pressure-sensitivity above normal ambient temperatures. It is generally recognized that styrene-butadiene polymers have poor heatsealable characteristics. From the discussion so far it is reasonable to expect that when the T_g of the polymeric stage is increased, the room temperature pressure-sensitivity can be eliminated, and heatselable polytelomer adhesive films can be obtained. In Figure 10 the heatsealability of a polymer and polytelomer are compared when the styrene/butadiene ratio of the polymeric stage is increased to 1.5. Both the polymer and polytelomer give non-tacky films at room temperature; when the polymer is used to laminate a polyester film to ABS plastic (10 sec, 30 psi), the bonds fail in an undesirable slip-stick fashion at low peel rates, and

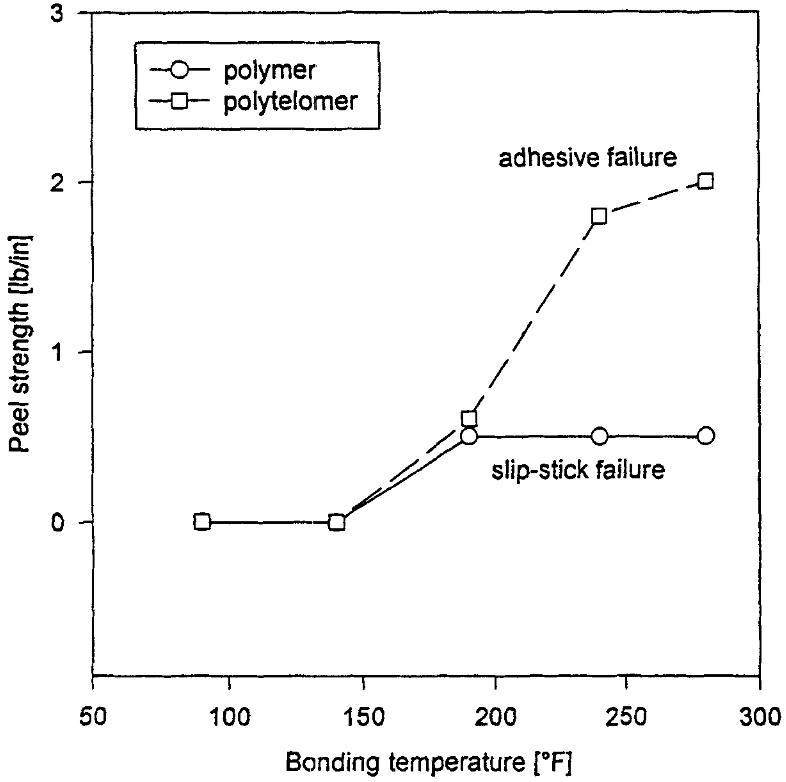


FIGURE 10 Heatsealability Evaluation.

essentially "fall-off" at high peel rates (glassy response of the adhesive film). When the polytelomer is used, then good bonds that fail smoothly with a measurable peel strength are obtained. In fact, the heatsealable temperature for the given time and pressure can be determined to be about 250 to 280°F. In this way the polytelomerization technology can be exploited to open new applications for styrene-butadiene monomers.

4. CONCLUSIONS

It has been shown that the novel polytelomerization technology described in this paper can provide new properties of styrene/butadiene copolymers. The most important factors that control the properties of final compositions are (i) the weight ratio of the polymeric and telomeric stages, (ii) the T_g and molecular weight of each stage, (iii) the level of carboxylation, and (iv) the degree of conversion of the polymeric stage. These compositions have been shown to have advantageous properties for pressure-sensitive, laminating and heatsealable applications.

Acknowledgements

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