

# Emulsion Copolymerization of *N*-Phenylmaleimide with Styrene

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## SYNOPSIS

Emulsion copolymerization of *N*-phenylmaleimide (PMI) with styrene (St) was conducted via semibatch and batch methods. The effect of monomer mixture composition and method of copolymerization on copolymer structure–property relationships was investigated. The semibatch copolymers have a homogeneous molecular structure, exhibiting a single  $T_g$  which increases linearly with increasing PMI content. The batch copolymers have a heterogeneous molecular structure, exhibiting two  $T_g$ 's, assigned to the polystyrene (PSt) and poly(PMI-co-St) components. The composition drift in the batch-copolymerized product, at different conversion levels, was examined by DSC and FTIR techniques. In general, the inherent viscosity of the semibatch copolymers is lower than that of the corresponding batch ones. The Young's modulus increases for the semibatch copolymers, with increasing PMI content, while a clear trend for the batch copolymers is not found. The tensile strength tends to decrease for both types of copolymers when PMI content increases. The thermal stability increases with increasing PMI content in the copolymers. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

There has been a considerable interest in the synthesis of copolymers containing maleimide moieties.<sup>1–5</sup> Such copolymers contain five-member planar rings in the chain, which hinder chain rotation, resulting in greater structural stiffness and higher thermal stability.

Solution copolymerization of *N*-aryl-substituted maleimides with other vinyl monomers such as styrene, methyl methacrylate, and vinyl acetate has been studied,<sup>5</sup> focusing on the copolymerization behavior. These copolymers tend to form an alternating structure when maleimides react with electron-donor comonomers, such as styrene, at low conversions, regardless of the monomers' feed composition. In such a case, the desired copolymer

structure and properties are difficult to be controlled by simply adjusting the monomers' composition.

Several patents<sup>6–8</sup> have described maleimide-involved emulsion copolymerization for the preparation of matrices for composite materials with a high heat-distortion temperature and high-impact properties. Recently, emulsion copolymerization of *N*-(2,4,6-tribromophenyl)maleimide (TBPMI) with styrene was investigated,<sup>9</sup> aiming at structure-controlled copolymers, combined with fire retardancy. It was found that the latex copolymerization procedure has a great influence on the copolymer structure and properties. For instance, semibatch copolymers were homogeneous, showing a single  $T_g$ , while the batch products were heterogeneous, exhibiting two  $T_g$ 's, corresponding to polystyrene (PSt) and poly(TBPMI-co-St) as two separate phases. In this work, copolymers of *N*-phenylmaleimide (PMI) and St were synthesized by emulsion semibatch and batch copolymerization methods. The effect of comonomers' ratio and polymerization method on copolymer chain structure, inherent viscosity,  $T_g$ , me-

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**Table I** Emulsion Copolymerization Formulation at 70°C<sup>a</sup>

Ingredients	Batch Process in Reactor	Semibatch Process		
		In Reactor	Funnel 1	Funnel 2
Monomers <sup>b</sup>	47.0 g			47.0 g
1% SLS <sup>c</sup>	30 mL	20 mL	10 mL	
Triton X-100 (18%)	25 mL	15 mL	10 mL	
DD-water <sup>d</sup>	82 mL	53 mL	25 mL	
3% K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3 mL		3 mL	
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> · 10H <sub>2</sub> O	0.05 g	0.05 g		

<sup>a</sup> Solid content is 25 wt %.

<sup>b</sup> Maximum PMI content is 50 wt %.

<sup>c</sup> Sodium lauryl sulfate.

<sup>d</sup> Distilled and deionized water.

chanical properties, and thermal stability were investigated.

## EXPERIMENTAL

### Materials

*N*-Phenylmaleimide (PMI) was supplied by Mitsui Toatsu Tokyo, Japan, and used as received. Styrene was twice washed with 5% NaOH aqueous solution before use. Sodium lauryl sulfate (Merck), Triton X-100 (Bio-Lab, Israel), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Merck), Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> · 10H<sub>2</sub>O (Merck), and *N,N*-dimethylformamide (Merck) were used as received.

### Emulsion Copolymerization

The copolymers were prepared through emulsion semibatch (gradual addition of monomers) and batch (single addition) copolymerization procedures using the formulations given in Table I. The detailed procedures were previously described.<sup>9</sup>

### Polymer Analysis

IR analysis was performed using a Mattson 1000 Fourier transform infrared (FTIR) spectrometer. Thin, transparent copolymer films were prepared by casting 0.4% dichloromethane solutions onto aluminum plates at room temperature, followed by solvent evaporation. Inherent viscosity was measured using an Ubbelohde viscometer and a 0.5 g/dL *N,N*-dimethylformamide solution at 30°C.

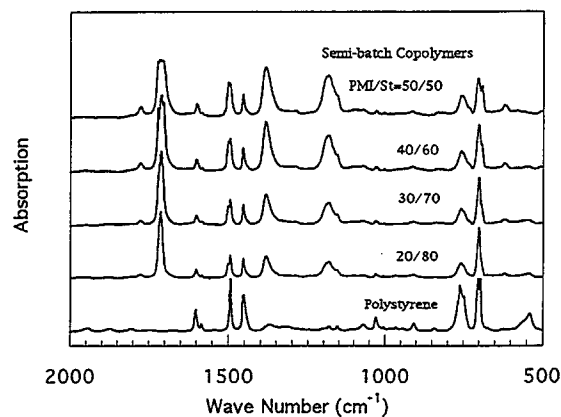
The glass transition temperature ( $T_g$ ) was measured using a Mettler TC 10A DSC. Samples, 12–18 mg, were scanned at a heating rate of 10°C/min under nitrogen. The  $T_g$  values were taken as the

transition midpoint of the second run. Thermal stability was studied using a Setaram TDA92 TGA, at a heating rate of 10°C/min, under an air atmosphere.

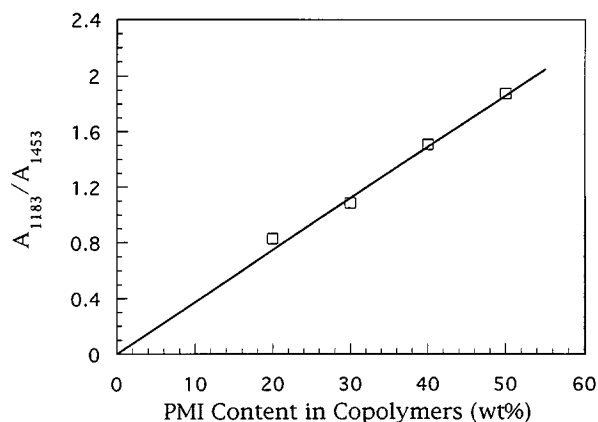
Specimens, 128 × 12.4 × (1.5–2.2) mm, for mechanical testing were prepared by compression molding. The mechanical properties were measured using a J. J. LLOYD, M30K tensometer at 23°C. The tensile and flexural (three-point bending with a 26 mm gauge length) behavior was measured at a crosshead speed of 1.0 mm/min.

## RESULTS AND DISCUSSION

FTIR spectra of the semibatch copolymers and of PSt are shown in Figure 1. Typical absorptions of the copolymer representing the PMI moiety are found at 1184 (C—N), 1384 (five-member ring), and 1710 cm<sup>-1</sup> (C=O). The characteristic absorptions of PSt are at 1453 and 1493 cm<sup>-1</sup>, reflecting the semicircle stretch and mixed C—H bending of



**Figure 1** FTIR spectra of semibatch copolymers.



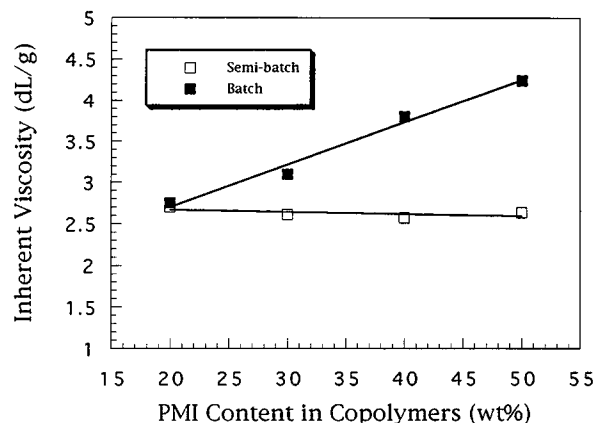
**Figure 2** Dependence of  $A_{1182}/A_{1453}$  on PMI content in semibatch copolymers.

a monosubstituted benzene ring. The intensity ratio of the 1182 and 1453  $\text{cm}^{-1}$  absorptions is found sensitive to composition and shows a linear dependency on PMI content, as in Figure 2. This dependence for the semibatch copolymers is expressed as follows:

$$A_{1183}/A_{1453} = 0.038 \text{ PMI (wt \%)}$$

It should be noted that the measured copolymer compositions are actually determined by the initially charged monomer compositions, since the monomers are almost fully consumed and the formed coagula are always negligible. Thus, this expression can be used to estimate the high-conversion copolymers' composition.

The inherent viscosity of the semibatch and batch copolymers is depicted in Figure 3. The inherent viscosity of the semibatch copolymers is composition-independent in the studied range, while the inherent viscosity of the batch copolymers, higher than that of semibatch ones, increases linearly with PMI content. This different behavior in the chain lengths between the semibatch and batch copolymers may stem from the different monomer feeding rates, resulting in different copolymerization rates. The inherent viscosity behavior of the PMI/St system is different from that of the TBPMI/St system, as previously reported.<sup>10</sup> For the TBPMI/St system, the inherent viscosity decreased with increasing TBPMI content for the semibatch and batch copolymers. It should be noted that TBPMI is less reactive than is PMI and bromine-containing compounds often undergo chain-transfer reactions.<sup>11</sup> However, an opposite conclusion was drawn from the TBPMI/St solution copolymerization experiments, in which the inherent viscosity of the co-



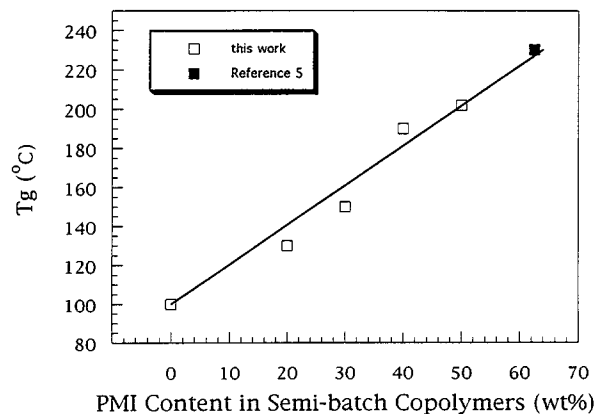
**Figure 3** Effect of PMI content on inherent viscosity of copolymers.

polymer increased with increasing TBPMI content in the monomer mixture.<sup>4</sup>

The semibatch copolymers exhibit a single  $T_g$ , which increases linearly with increasing PMI content, as shown in Figure 4, reflecting their relatively homogeneous molecular structure. The linear relationship between  $T_g$  and PMI content within the composition range studied is expressed as follows:

$$T_g(^{\circ}\text{C}) = 2.0 \text{ PMI (wt \%)} + 100$$

The  $T_g$  value is thus enhanced by about  $2.0^{\circ}\text{C}$  per 1 wt % of PMI. This equation suggests that the semibatch emulsion copolymerization method enables one to control the copolymer structure and properties by adjusting the monomer compositions. In comparison, the solution copolymerization always results in alternating copolymers, regardless of monomer composition. The batch copolymers, contrary to the semibatch ones, exhibit two  $T_g$ 's, indicating their heterogeneous nature, as shown in Table



**Figure 4** Effect of PMI content on  $T_g$  of copolymers.

**Table II**  $T_g$  of PMI/St Batch Copolymers ( $^{\circ}\text{C}$ )

PMI Content (Wt %)	$T_{g_1}$ ( $^{\circ}\text{C}$ )	$T_{g_2}$ ( $^{\circ}\text{C}$ )
20	103	208
30	100	208
40	101	211
50	117	209

II. The lower  $T_g$ , ca.  $103^{\circ}\text{C}$ , represents PSt chains, whereas the higher one, ca.  $210^{\circ}\text{C}$ , represents poly(PMI-co-St) of a roughly constant composition, probably due to a charge-transfer complex mechanism. The PMI content in the poly(PMI-co-St) component is estimated as 55 wt % (42 mol %), corresponding to a  $T_g$  of  $210^{\circ}\text{C}$ . Thus, PMI and St form nearly alternating-structured segments using a wide range of monomer feed compositions in batch copolymerization.

In solution polymerization, PMI and St have a strong tendency to complex and form alternating copolymers rather than to form random copolymers or homopolymers of the individual monomers.<sup>5</sup> A strong tendency for alternation<sup>12</sup> is also depicted by the copolymerization reactivity ratios  $r_1 = 0.047$  and  $r_2 = 0.012$  for styrene ( $M_1$ ) polymerization with PMI ( $M_2$ ). In aqueous emulsion batch copolymerization, all the monomer mixture is charged into the reactor and, thus, chain growth is a competitive process between cross-propagation (PMI-St) and homopolymerization (St-St or PMI-PMI) reactions. In the aqueous emulsion polymerization conditions, the formation of a PMI-St complex is very unlikely. The dominating parameters are the relative monomer diffusion rates through the water to the monomer-polymer particle and the relative copolymerization rates. Since PMI does not homopolymerize and its tendency to add to a styrene radical is faster than that of styrene to the styrene radical, an alternating copolymer structure is formed, provided that PMI diffuses faster than does styrene from the monomer reservoirs to the monomer-polymer particles. The main difference between the present batch and semibatch methods is that in the latter, at sufficiently low monomer mixture feeding rates, the reaction proceeds under monomer-starved conditions which are the dominating factor, yielding the homogeneous copolymer structures showing a single  $T_g$ , increasing with PMI. Thus, cross-propagation predominates during chain growth, and nearly alternating copolymer chains are first formed. When the PMI concentration in the monomers' mixture becomes low, St-St reactions are more sig-

nificant; hence, PSt chains are then formed. This explains the DSC data, which identify two  $T_g$ 's, reflecting essentially two phase-separated domains. Since the batch copolymer has a heterogeneous chain structure, a drift in copolymer composition is expected and can be monitored by DSC and FTIR analysis at different conversion levels, as previously reported.<sup>9</sup>

Table III summarizes the conversion, composition, and  $T_g$  data for a batch copolymer at different reaction times. It should be noted that the conversion is significantly enhanced by increasing PMI content, in agreement with the previous discussion. Thus, the reaction temperature, in this case, had to be reduced from  $70$  to  $60^{\circ}\text{C}$  to control the conversion at the initial polymerization period. It can be seen that 56% conversion was obtained after only 5 min reaction time. DSC results indicate that copolymers at the initial polymerization period only exhibit a single  $T_g$ , at about  $220^{\circ}\text{C}$ , attributed to the PMI/St-formed alternating copolymer. The additional second  $T_g$ ,  $104^{\circ}\text{C}$ , assigned to PSt, appears only after about a 30 min reaction time, when the PMI concentration has become too low to generate an alternating copolymer. FTIR analysis also confirms the composition drift in batch copolymerization. The PMI content in the copolymer is higher than in the charged monomer composition in the early reaction stage, and it continuously decreases as copolymerization progresses. Interestingly, even a third  $T_g$ , related to St-rich chains, is identified by DSC, although it does not show up in the final product. Thus, the final high-conversion product is roughly a mixture of PSt and an almost alternating copolymer.

Mechanical property results are summarized in Table IV. The Young's modulus of the semibatch

**Table III** Effect of Reaction Time on Copolymer Conversion, Composition, and  $T_g$ 

Time (min)	Conversion (Wt %)	PMI Content (Wt %)	$T_{g_1}$ ( $^{\circ}\text{C}$ )	$T_{g_2}$ ( $^{\circ}\text{C}$ )
5	56	—	N	221
10	67	55	N	220
15	—	51	N	221
20	75	—	N	221
30	—	—	N	221
45	85	44	104	219
60	88	43	100 (159)	205
120	92	—	104 (126)	214
240	> 98	37	104	220

N: no  $T_g$  detected.

**Table IV Mechanical Properties of Semibatch and Batch PMI/St Copolymers**

PMI Content (Wt %)	Process	Tensile Strength (MPa)	Young's Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
PSt	Semibatch	43	3450	86	2480
20	Semibatch	23	2950	58	3280
30	Semibatch	20	3250	47	3350
50	Semibatch	16	3650	49	3320
PSt	Batch	32	3700	73	3000
20	Batch	16	3560	47	3755
30	Batch	16	3400	39	3825
50	Batch	6	3440	27	3210

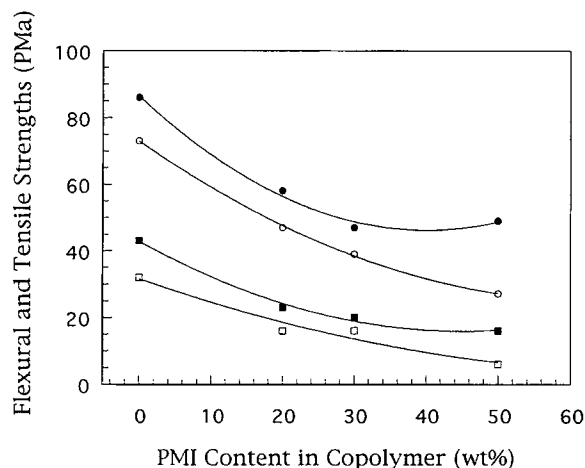
copolymers increases with increasing PMI content, due to the increasing chain stiffness, while tensile strength tends to decrease when PMI content increases. The Young's modulus of the batch copolymers is roughly constant and the tensile strength decreases with increasing PMI content. The flexural moduli of both the semibatch and batch copolymers increase, while the flexural strength decreases compared with neat PSt, again due to the increasing brittleness. The semibatch copolymers have higher tensile and flexural strengths than those of the batch ones, as shown in Figure 5, reflecting the difference in molecular structure, as previously described. The mechanical properties of the PMI/St system are similar to those of the TBPMI/St system.<sup>9</sup>

Figure 6 depicts thermal gravimetric analysis (TGA) curves of semibatch copolymer samples. It can be seen that the thermal stability of the copolymer increases with increasing PMI content, due to

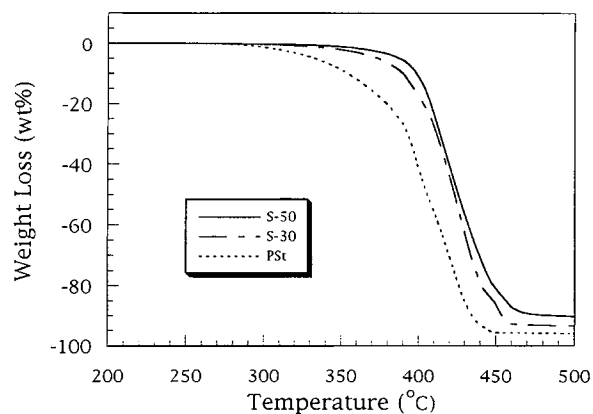
the presence of the five-member planar rings of the PMI moiety in the copolymer.

## CONCLUSIONS

Semibatch and batch emulsion copolymerization of PMI with St produces copolymers of different structure and properties. A semibatch copolymer has a homogeneous chain structure; its  $T_g$  increases linearly with increasing PMI content, while a batch copolymer has a heterogeneous chain structure roughly consisting of poly(PMI-*co*-St) and PSt components, as evidenced by their individual  $T_g$ 's. PMI content is estimated as 42 mol % in the poly(PMI-*co*-St) segment, showing a trend to form alternating chain structures in batch copolymerization. Compared with its batch counterpart, a semibatch copolymer has a lower inherent viscosity and higher tensile and flexural strengths. The thermal stability increases with increasing PMI content in the copolymer.



**Figure 5** Effect of PMI content on mechanical properties: (●) flexural strength of semibatch copolymers; (○) flexural strength of batch copolymers; (■) tensile strength of semibatch copolymers; (□) tensile strength of batch copolymers.



**Figure 6** Thermogravimetry of the semibatch copolymers.

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