Synthesis and Thermoanalysis of Emulsion Terpolymers of *N*-Phenylmaleimide, Styrene, and Acrylonitrile

LITING YANG,[1] LIUCHENG ZHANG,[1] GUODONG LIU,[1] JUNGANG GAO,[1] SEN YANG,[1] MINGSHAN YANG,[2] RIGUANG JIN[2]

[1] Department of Chemistry, Hebei University, Baoding 071002, People's Republic of China

[2] Material and Engineering College of Beijing University of Chemical and Technology, Beijing 100029, People's Republic of China

ABSTRACT: Terpolymers of *N*-phenylmaleimide (PMI), styrene, and acrylonitrile (AN) were synthesized by emulsion polymerization. The thermal properties of terpolymers at different PMI and AN feed contents were investigated by differential scanning calorimetry, torsional braid analysis, thermogravimetric analysis, and a Vicat softening point test. The results showed the glass-transition temperature and decomposition temperature of the terpolymers increased with increasing PMI feed content. Furthermore, the Vicat softening point of the terpolymers rose with PMI feed content. The weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of the terpolymers were also determined by gel permeation chromatography. The results showed that the $\bar{M}_w$ and $\bar{M}_n$ of the terpolymers decreased with increasing PMI feed content and increased with increasing AN feed content. The mechanical properties (tensile strength and impact strength) of the terpolymers decreased with increasing PMI feed content and increased with increasing AN feed content. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1067–1073, 2001

Key words: *N*-phenylmaleimide; styrene; acrylonitrile; emulsion polymerization; thermoanalysis

INTRODUCTION

There has been considerable interest in the synthesis of copolymers containing maleimide moieties, especially of *N*-phenylmaleimide (PMI).[1–5] 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 PMI with other vinyl monomers such as styrene (St), methyl methacrylate, and vinyl acetate were studied,[5]

focusing on the copolymerization behavior. These copolymers tend to form an alternating structure when PMI reacts with electron-donor comonomers, such as St, at low conversions, regardless of the monomers' feed composition. In such a case the desired copolymer structure and properties are difficult to control by simply adjusting the monomers' composition.

Recently, emulsion copolymerization of *N*-aryl-substituted maleimide and other vinyl monomers, such as St, were investigated[4–6] to find structure-controlled copolymers. It was found that the latex copolymerization procedure has great influence on the copolymer structure and properties. For instance,[4] semibatch copolymers (gradual addition of monomers) were homogeneous, showing a

Table I   Recipe of Monomers in Copolymerization (wt %)

	0	1	2	3	4	5	A	B	C	D	E
AN	23.5	22.4	21.2	20	18.8	17.6	0	10	20	30	40
PMI	0	5	10	15	20	25	20	18	16	14	12
St	76.5	72.6	68.8	65	61.2	57.4	80	72	64	56	48

The 0–5 St/AN was fixed at 3.25/1, and A–E St/PMI was fixed at 4/1. The solid content is 40 wt %, the SLS content is 3 wt % monomers, and the $K_2S_2O_8$ content is 0.5% monomers.

single glass-transition temperature (T_g), while the batch products (single addition of monomers) were heterogeneous, exhibiting two T_g's, corresponding to polystyrene (PSt) and poly(PMI-*co*-St) as two separate phases. But there are no reports on the thermal and mechanical properties of PMI containing terpolymers. In this work terpolymers of PMI, St, and acrylonitrile (AN) were synthesized by the semibatch emulsion copolymerization method. The effects of the monomer com-

position on the weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$), T_g, thermal stability, and mechanical properties were investigated.

EXPERIMENTAL

Materials

The PMI was synthesized from maleic anhydride and aniline according to the literature.[7] The St and AN were washed twice with a 5% NaOH aqueous solution before use. Sodium lauryl sulfate (SLS), $K_2S_2O_8$, and $Al_2(SO_4)_3$ were AR grade (Beijing Chemical Reagent Co.). The water used in all the experiments was distilled and deionized water.

Emulsion Copolymerization

A solution of SLS was placed in a 100-mL four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct; it was stirred for 30 min under nitrogen and then the monomer mixture was gradually added at 75–
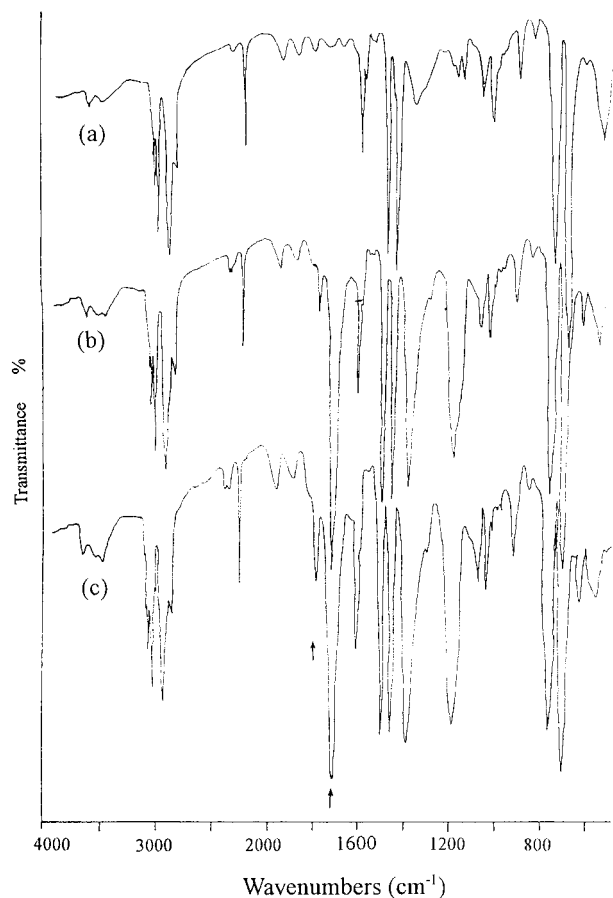

Figure 1   FTIR spectra of the terpolymers at different feed compositions of PMI:St:AN: 0:76.5:23.5 (spectrum a), 15:65:20 (spectrum b), and 25:57.4:17.6 (spectrum c).

Table II   Elemental Analysis Results

PMI:St:AN	
Feed Ratio	Test Value
0:76.5:23.5	0:76.45:23.55
5:72.6:22.4	5.92:71.78:22.3
10:68.8:21.2	10.58:68.32:21.1
15:65:20	14.95:64.86:20.19
20:61.2:18.8	19.19:62.1:18.71
25:57.4:17.6	23.14:59.68:17.18
20:80:0	20.42:79.48:0
18:72:10	18.11:70.67:11.22
16:64:20	16.49:63.28:20.23
14:56:30	14.33:55.37:30.3
12:48:40	11.79:48.11:40.1

Table III $\bar{M}_w$ and $\bar{M}_n$ of Terpolymers at Different PMI Feed Contents

	PMI Feed Content (wt %)					
	0	5	10	15	20	25
$\bar{M}_w \times 10^{-4}$	19.16 ± 0.16	19.15 ± 0.13	18.74 ± 0.07	18.33 ± 0.04	17.85 ± 0.11	16.98 ± 0.07
$\bar{M}_w/\bar{M}_n$	3.06	3.41	2.81	3.03	3.73	2.83

80°C during 1 h. After that the reaction system was held at 80–85°C for another 1.5 h. The $K_2S_2O_8$ was used as the initiator. When the reaction was completed, the product was obtained by pouring it into a solution of 2% $Al_2(SO_4)_3$, filtering, washing, and drying under a vacuum. The products were purified by extraction with methanol and drying under a vacuum. The conversion ratios of the monomers in all copolymerizations were over 95%. The semibatch copolymerization procedures were performed using the recipes given in Table I.

Copolymer Analysis

Samples were dried in a high vacuum drying oven at 60°C for 24 h.

The copolymer molecular weight was measured using a P200 gel permeation chromatography (GPC) apparatus. Tetrahydrofuran was used as the flowing phase, and the flow rate was 1 mL/min. The column was calibrated by using commercially available narrow-distribution PSt. The $\bar{M}_w$ and $\bar{M}_n$ were calculated by

$$\bar{M}_w = \frac{\sum_i H_i M_i}{\sum_i H_i} \quad \bar{M}_n = \frac{\sum_i H_i}{\sum_i \dfrac{H_i}{M_i}}$$

where H is the height of the GPC spectrum.

Thermogravimetric analysis (TGA) was carried out by means of a Shimadzu DT-40 thermogravimeter. The half-weight loss temperature (T_{50}) was obtained when the weight loss of the copolymer reached 50% at a heating rate of 10°C/min in an air atmosphere.

The copolymer T_g was measured using a Shimadzu DT-40 differential scanning calorimetry (DSC) instrument with α-Al_2O_3 as the reference material at a heating rate of 20°C/min under nitrogen. The $T_{g\text{DSC}}$ value was taken from the midpoint of the temperatures of the initial and final tangents in the DSC traces.[8]

The T_g of the copolymer was also measured using a GDP-3 torsional braid analysis (TBA) unit at a heating rate of 2°C/min. The $T_{g\text{TBA}}$ was taken from the maximum logarithmic decrement in amplitudes per cycle (Δ).

The mechanical property test was carried out using a tensile strength tester and an impact strength tester.

The copolymers' structure change was investigated by using an FTS-40 IR spectrophotometer. The compositions of the copolymers were determined using a PE-2400 elemental analyzer.

RESULTS AND DISCUSSION

Structure and Composition

The IR spectra of PMI-St-AN at different monomer feed proportions are shown in Figure 1. With the incorporation of PMI, the most significant feature is the increase of the double absorption peak at 1780 and 1710 cm^{-1} of the $\nu_{C=O}$ of PMI (marked by an arrow). It is observed that the double absorption peak of the $\nu_{C=O}$ of PMI grad-

Table IV $\bar{M}_w$ and $\bar{M}_n$ of Terpolymers at Different AN Feed Contents

	AN Feed Content (wt %)				
	0	10	20	30	40
$\bar{M}_w \times 10^{-4}$	26.18 ± 0.30	31.41 ± 0.66	35.70 ± 0.39	33.77 ± 0.41	35.73 ± 0.44
$\bar{M}_w/\bar{M}_n$	3.16	2.84	2.82	2.64	2.48

Table V   Glass-Transition and Decomposition Temperatures by DSC, TBA, and TGA of Copolymers at Different PMI Contents

	PMI Feed Content (wt %)					
	0	5	10	15	20	25
$T_{g\mathrm{DSC}}$ (°C)	87.2	116.3	118	120.9	123.4	126
$T_{g\mathrm{TBA}}$ (°C)	104.2	114.5	121.7	129.8	127.8	136.2
T_{50} (°C)	374.6	377.0	378.0	376.5	381.1	381.1

ually increases with the increasing PMI feed content. When no PMI is fed, there is no absorption at 1780 and 1710 cm^{-1} on the FTIR spectrum. This indicates that the PMI content in the copolymer increased with the increasing PMI feed content.

The elemental analysis (Table II) shows that the composition of the terpolymers is almost the same as the feed composition. The results show that the monomers are almost fully consumed and the formed coagula are always negligible. Thus, the monomer feed composition can be used to estimate the terpolymer composition.

Molecular Weights

The $\bar{M}_w$ and $\bar{M}_n$ of the PMI-St-AN emulsion copolymers at different PMI feed contents (St:AN was fixed at 3.25:1) and different AN feed contents (St:PMI was fixed at 4:1) are shown in Tables III and IV. Both tables show that the $\bar{M}_w$ and $\bar{M}_n$ decrease with increasing PMI content and increase with increasing AN content.

Previous studies showed that there was a maximum copolymerization rate at f_{St} (styrene monomer mole fraction) ≈ 0.3 in solution copolymerization of St with PMI because of the nearly alternating copolymerization behavior and the existence of a charge-transfer complex.[9] The molecular weight model of the St-PMI solution co-

polymer, which also showed a maximum value at the proper St/PMI ratio, was also obtained.[10]

It is known that the polymerization reaction mainly takes place in micelles in emulsion polymerization and only one active radical can be tolerated in it, so the micelle will contain either one or zero radicals at any one time. The rate of the "on–off switching" is controlled by both the rate of radical production and the number of micelles in the reaction medium. So, for a fixed initiator concentration and temperature, the chain length, and thus the molecular weight, of the polymer is a function of the rate of radical propagation ν_p and is not affected by other effects.[11] Furthermore, ν_p is a function of the monomer feed ratio if the reactivity ratios are fixed; it will be a maximum at the proper monomer ratio as reported. Thus, the molecular weight of the copolymer was mainly affected by the monomer feed composition when the copolymerization temperature, emulsifying agent, and initiator concentrations are fixed and should be a maximum at the proper monomer ratio. However, in this study the polymerization was under a monomer starved condition (gradual addition of monomers), so the

Table VI   Glass-Transition and Decomposition Temperatures by DSC, TBA, and TGA of Copolymers at Different AN Contents

	AN Feed Content (wt %)				
	0	10	20	30	40
$T_{g\mathrm{DSC}}$ (°C)	134.3	120.9	113.7	113.9	102
$T_{g\mathrm{TBA}}$ (°C)	138.3	137.0	132.8	132.2	126.3
T_{50} (°C)	364.6	370.5	380.3	382.5	397.5
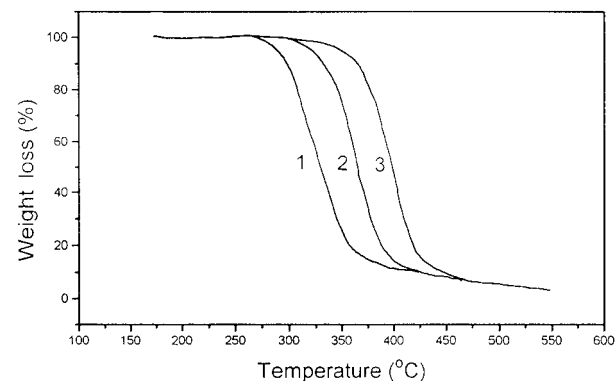
Figure 2 TGA curves of the copolymers: PSt (curve 1), 80:20:0 St:PMI:AN (curve 2), and 16:64:20 St:PMI:AN (curve 3).
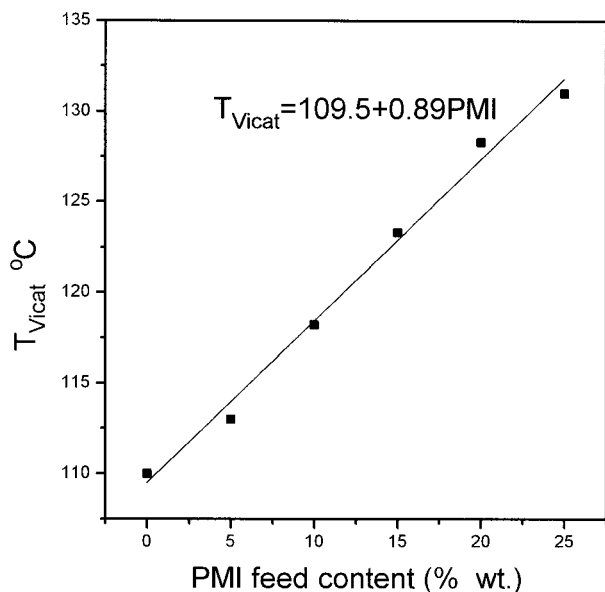
Figure 3 The relationship of the T_{Vicat} and PMI feed content.

ν_p was a function of the reaction activity of the radical. The results are thus different from that of solution copolymerization. The reaction activity of PMI$^\bullet$ is smaller than the St$^\bullet$ and AN$^\bullet$ radicals. The monomer feed compositions are shown in Table II. As the feed content of the PMI increases from zero to 25 wt %, the feed content of the St plus AN decreases from 100 to 75 wt %. So, the concentration of PMI$^\bullet$ should increase with the increasing PMI feed content and the concentration of St$^\bullet$ and AN$^\bullet$ should decrease with the increasing St and AN feed contents. Therefore, the ν_p decreases with the increasing PMI feed content, and the molecular weight also decrease with the increasing PMI feed content. This is the reason that the average molecular weight of the PMI-St-AN emulsion terpolymers decreases with increasing PMI feed content and increases with increasing AN feed content.

TGA

The thermal stability of the copolymer was arbitrarily defined as a function of the initial thermal stability temperature (T_i) and the T_{50} at particular environmental conditions described previously. The experimental results are given in Tables V and VI. Some thermograms of the studied series of copolymers are shown in Figure 2 for the purpose of comparison.

Many studies showed that is PSt liable to decompose at high temperature. The T_i and T_{50} of

PSt were found to be 269.3 and 329.3°C, respectively, in our study. The results in Tables V and VI indicate that the thermal stability tends to increase as the PMI and AN feed contents increase. The copolymers' T_{50} increased with the increasing PMI or AN feed content. The T_i and T_{50} increased to 26.0 and 35.3°C, respectively, when PSt was copolymerized with 20 wt % PMI, because of the presence of 1,2-ethylenic units directly linked to the St units.[5] The decomposition temperature of the copolymers increased with increasing PMI content, because of the five-member planar ring in the chain. The T_i and T_{50} of PMI-St-AN (25:57.4:17.6) was 36.6 and 51.8°C higher, respectively, than neat PSt, and the decomposition temperature also increased with the increasing AN feed content. The intermolecular reaction of PolyAN at about 200°C will produce six-member rings in the molecular chain.[12] These chain segments possess a higher decomposition temperature, which highly restrains the decomposition reaction of PSt. The sequence length of the AN chain segment will increase while the AN feed content increases. Thus, the incorporation of PMI and AN into St in emulsion copolymerization will highly restrain the decomposition reaction of PSt.

Glass-Transition Temperature

The copolymers' T_g was another important indication of its thermal properties, and their values
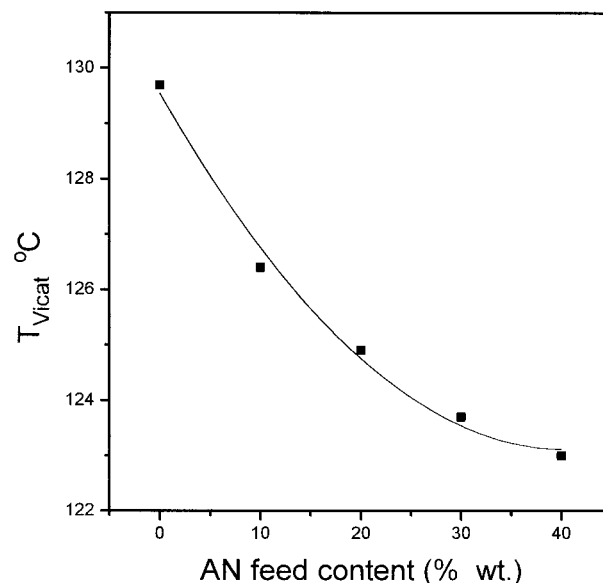

Figure 4 The relationship of the T_{Vicat} and AN feed content.

Table VII   Mechanical Properties of Terpolymers at Different PMI Feed Contents

	PMI Feed Content (wt %)					
	0	5	10	15	20	25
Tensile strength (MPa)	56.2	50.0	46.0	43.7	41.8	40.3
Impact strength (kJ/m^2)	2.61	2.43	2.22	1.90	1.86	1.78

were determined by DSC and TBA and are shown in Tables V and VI. The results show that the copolymers' T_g increases with increasing PMI feed content while decreasing with increasing AN feed content, although there are differences between the DSC and TBA results.

An interesting fact can be found from Tables V and VI: obviously the $T_{g\text{TBA}}$ is higher than the $T_{g\text{DSC}}$ for the same sample. This is due to the different test frequencies of the two different locating T_g methods. As is known, the test frequency of DSC (a static method) is about 10^{-3} Hz, which is much lower than 0.5 Hz, the test frequency of TBA (a dynamic method).[13]

It should be noted that the single T_g of the terpolymers is mainly due to the semibatch method. The main difference between the batch and semibatch methods is that in the latter, at sufficiently low monomer mixture feeding rates, the reaction proceeds under monomer starved conditions, which is the dominating factor, yielding the homogeneous copolymer structures showing a single T_g, that increases with the PMI.

The Vicat softening temperatures of the terpolymers are shown in Figures 3 and 4. As seen from Figure 3, the Vicat softening temperatures of the terpolymers increase linearly with increasing PMI feed content. The linear relationship between the T_{Vicat} and PMI feed content is expressed as follows:

$$T_{\text{Vicat}} = 109.5 + 0.89 \text{ PMI (wt \%)}$$

The T_{Vicat} value is thus enhanced by about 0.89°C per 1 wt % of PMI. But the T_{Vicat} of the terpolymers, as seen from Figure 4, decreases with increasing AN feed content.

The T_g and T_{Vicat} reflect the stiffness and the movement ability of the molecular chain segments. A PMI containing terpolymer contains five-member planar rings in the chain, which hinder chain rotation, resulting in greater structural stiffness. So, the T_g and the T_{Vicat} of the terpolymers increase with the increasing of the PMI feed content. The PMI feed content will decrease while the AN feed content increases. This will result in a decrease of the spatial obstruction of internal rotation and a decrease in the structural stiffness of the molecular chain. This is the reason that the T_g and T_{Vicat} decrease with the increase of the AN feed content.

Mechanical Properties

The mechanical properties of terpolymers at different feed proportions are summarized in Tables VII and VIII. Table VII shows that the tensile strength decreases by 16 MPa and the impact strength drops 32% as the PMI feed content increases from zero to 25 wt %. The PMI containing terpolymer contains five-member rings in the chain, and this ring contains a large bigroup (phenyl group). So, the interaction of the molecular chain will decrease with increasing PMI content, which results in lower tensile strength. The stiffness of the molecular chain increases with the increasing PMI feed content. This is the reason that the impact strength decreases with the increasing PMI feed content.

However, the tensile strength and the impact strength of the terpolymers, as seen in Table VIII,

Table VIII   Mechanical Properties of Terpolymers at Different AN Feed Contents

	AN Feed Content (wt %)				
	0	10	20	30	40
Tensile strength (MPa)	9.52	30.1	49.0	50.0	53.6
Impact strength (kJ/m^2)	1.15	1.64	1.76	1.86	1.93

increase with increasing AN feed content. The tensile strength of poly(PMI-*co*-St) (monomer feed composition = 20:80) is 9.52 MPa, and it will rise to 49 MPa when the feed ratio of St:PMI:AN is 16:64:20. The interaction of the molecular chain increased when AN was introduced, which was due to the increasing flexibility of the chain segments, and the impact strength increased 70% when the AN feed content was 40 wt %. This was mainly due to the decrease of the molecular chain stiffness. The result shows that AN is a useful monomer for improving the mechanical properties of PMI containing copolymers and is also useful for the thermal properties of the target copolymers.

CONCLUSIONS

According to the experimental results, four conclusions can be made.

1. Semibatch emulsion copolymerization of PMI, St, and AN produces copolymers of homogeneous chain structure, as evidenced by their single T_g.
2. The composition of the semibatch copolymers is almost the same as the feed composition.
3. PMI is an effective monomer for improving the thermal properties of PSt, especially the glass-transition and decomposition temperatures.
4. The AN chain segment is useful for the

mechanical properties of poly(St-*co*-PMI). The suitable content should be in the range of 10–15%.

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