

Synthesis and Thermal Analysis of Emulsion Terpolymers of *N*-Phenylmaleimide, Methyl Methacrylate, and Acrylonitrile

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ABSTRACT: Terpolymers of *N*-phenylmaleimide (PMI), methyl methacrylate (MMA), and acrylonitrile (AN) were synthesized by emulsion polymerization. The thermal properties of the terpolymers, at different PMI and AN feed contents, were investigated by TBA, TGA, and the Vicat softening point test. The results show that the glass transition temperature (T_g) and decomposition temperature of the terpolymers increase with increasing PMI feed content. Furthermore, the Vicat softening points of the terpolymers increase with the PMI feed content. The \bar{M}_w and \bar{M}_n of the terpolymers were also determined by GPC. The results show that the \bar{M}_w and \bar{M}_n of the terpolymers have a maximum value in the range of 0–30% PMI feed content and decrease with an increasing AN feed content. The mechanical properties (tensile strength and impact strength) of the terpolymers decrease with an increasing PMI feed content and increase with an increasing AN feed content. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2455–2462, 2001

Key words: PMI; MMA; AN; emulsion polymerization; thermal analysis

INTRODUCTION

Poly(methyl methacrylate) (PMMA) has many excellent properties, such as colorlessness, high light transmittance, chemical resistance, weathering, and corrosion resistance, and dimensional stability; therefore, it is employed for various applications in glazing and optical use. However, PMMA has low heat-resistance and its heat-deflection temperature is as low as 96°C. Recently, further improvement in the heat-resistant property has been strongly desired.

There has been considerable interest in the synthesis of copolymers containing maleimide

moieties, especially *N*-phenylmaleimide (PMI),^{1–5} aiming at improving the heat resistance. Such copolymers contain five-member planar rings in the chain, which hinder chain rotation, resulting in greater structural stiffness and higher thermal stability.

Solution copolymerizations of PMI with other vinyl monomers such as styrene, methyl methacrylate, and vinyl acetate have been studied,⁵ focusing on the copolymerization behavior. These copolymers tend to form an alternating structure when PMI reacts 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 control by simply adjusting the monomers' composition.

Recently, emulsion copolymerization of *N*-aryl-substituted maleimide and other vinyl monomers,

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Table I Recipe of Monomers in Copolymerization (in Weight)

	No.												
	0	1	2	3	4	5	6	A	B	C	D	E	F
AN	5	5	5	5	5	5	5	0	5	10	15	20	25
PMI	0	5	10	15	20	25	30	20	20	20	20	20	20
MMA	95	90	85	80	75	70	65	80	75	70	65	60	55

Solid content is 40 wt %. SLS content is 3 wt % of monomers. $K_2S_2O_8$ content is 0.5% of monomers.

such as styrene, was investigated,^{4–6} aiming at structure-controlled copolymers. It was found that the latex copolymerization procedure has a great influence on the copolymer structure and properties. For instance,⁴ semibatch copolymers (gradual addition of monomers) were homogeneous, showing a single T_g , while the batch products (single addition of monomers) were heterogeneous, exhibiting two T_g 's, corresponding to polystyrene and poly(PMI-co-St) as two separate phases. But there are no reports on the thermal properties and mechanical properties of PMI-containing terpolymers. In this work, terpolymers of PMI, methyl methacrylate (MMA), and acrylonitrile (AN) were synthesized by the semibatch emulsion copolymerization method. The effects of the monomers' compositions on the \bar{M}_w , \bar{M}_n , T_g , thermal stability, and mechanical properties were investigated.

EXPERIMENTAL

Materials

PMI was synthesized from maleic anhydride and aniline according to ref. 7. MMA and AN were twice washed 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 Regent Co., Beijing, China). The water used in all the experiments was distilled and deionized water (DDW).

Emulsion Copolymerization

A solution of SLS was placed in a 100-mL four-necked flask, equipped with a stirrer, thermometer, condenser, and nitrogen duct, stirring for 30 min under nitrogen, and then the monomer mixture was added gradually at 75–80°C during 1 h. After that, the reaction system was held at 80–85°C for another 1.5 h. $K_2S_2O_8$ was used as the

initiator. When the reaction was completed, the product was obtained by pouring into a solution of 2% $Al_2(SO_4)_3$, filtering, washing, and drying under a vacuum. The products were purified by extract with methanol and drying under a vacuum. The conversion ratios of the monomers in all copolymerizations were over 95%. The semibatch (gradual addition of monomers) and batch (single addition of monomers) copolymerization procedures' recipes are given in Table I.

Copolymer Analysis

The copolymers' structure change was investigated by using an FTS-40 IR spectrophotometer. The composition of the copolymers were determined using a PE-2400 elemental analyzer. Samples were dried in a high-vacuum drying oven at 60°C for 24 h.

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

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

where H is the height of the GPC spectrum.

Thermogravimetric analysis was carried out using a Shimadzu DT-40 thermograph (TG). The half-loss weight 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 glass transition temperature of the copolymer was measured using a GDP-3 torsional braid analyzer (TBA) at a heating rate of 2°C/min. T_g was taken from the maximum of the logarithmic

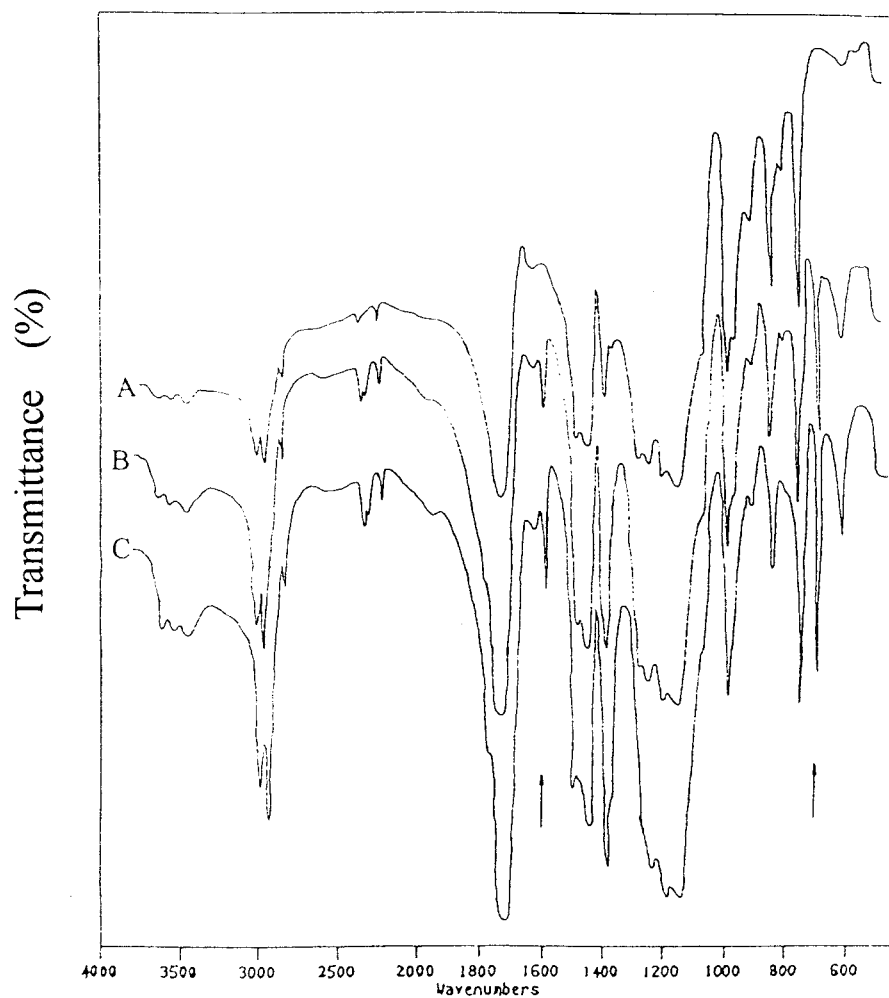


Figure 1 FTIR spectra of terpolymers at different feed compositions. Feed composition of PMI : MMA : AN: (a) 0 : 95 : 5; (b) 10 : 85 : 5; (c) 20 : 75 : 5.

mic decrement in amplitude per cycle Δ . The Vicat softening point was measured using a Vicat softening point tester at a heating rate of $2^{\circ}\text{C}/\text{min}$. The mechanical property tests were carried out using a tensile strength tester and an impact strength tester.

RESULTS AND DISCUSSION

Composition of Terpolymers

The IR spectra of PMI-MMA-AN (semibatch product) at different monomer feed proportions are shown in Figure 1. With the incorporation of PMI, the most significant feature is an increase of the absorption peaks at 1600 and 700 cm^{-1} of the single-substituted benzene group of PMI (marked by an arrow). It can be observed that the absorp-

tion peaks at 1600 and 700 cm^{-1} gradually increase with an increasing PMI feed content. With no PMI feed, there is no absorption at 1600 and 700 cm^{-1} in the FTIR spectrum, indicating that the PMI content in the copolymer increased with an increasing PMI feed content.

Elemental analysis of the semibatch products (seen in Table II) shows that the composition of the terpolymers is almost the same as that of the feed composition. This result shows 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 terpolymers' composition.

Molecular Weight

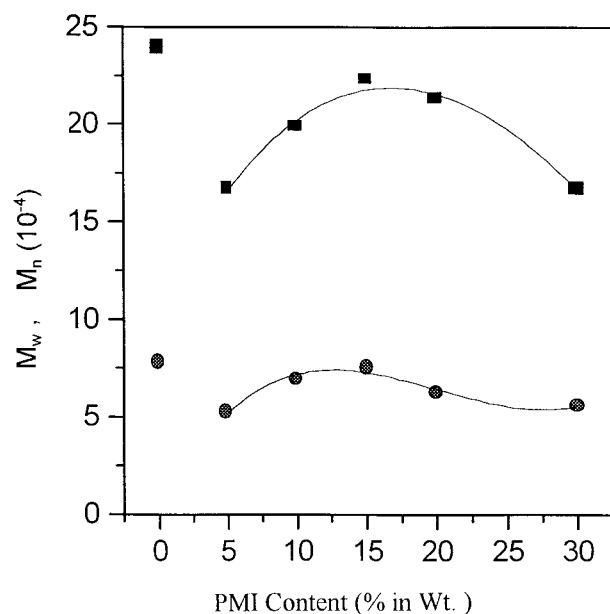
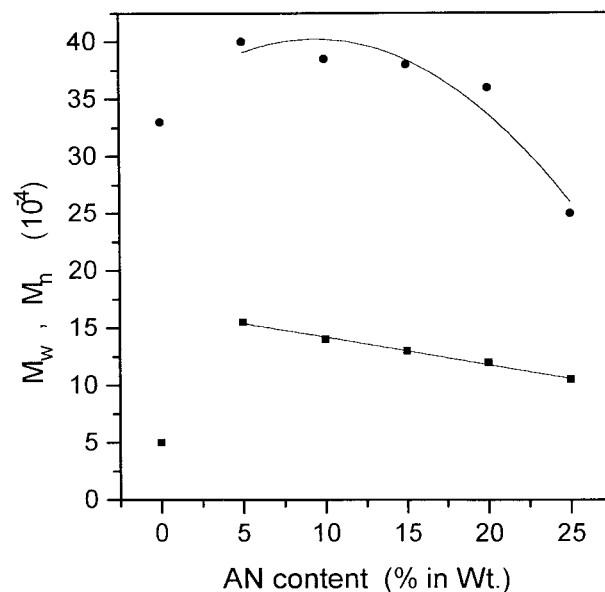
The \bar{M}_w and \bar{M}_n of the PMI-MMA-AN emulsion copolymers (batch and semibatch products) at dif-

Table II Elemental Analysis Results

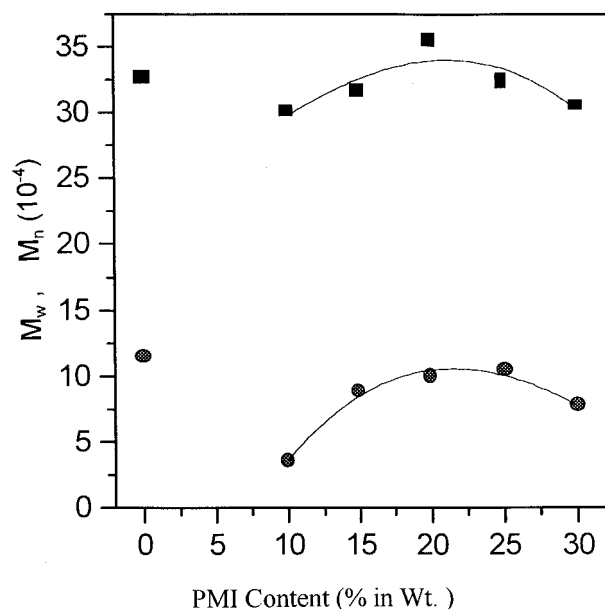
PMI : MMA : AN (Calculated Results)	PMI : MMA : AN (Experimental Results)
0 : 95 : 5	0 : 94.24 : 5.64
20 : 75 : 5	20.5 : 75.1 : 4.46
20 : 80 : 0	19.35 : 80.65 : 0
20 : 65 : 15	20.36 : 65.95 : 13.08
20 : 55 : 25	19.73 : 55.51 : 24.85

ferent PMI and AN feed contents are shown in Figures 2–5. As seen from Figures 2–5, both \bar{M}_w and \bar{M}_n have a maximum value with the PMI content between 5 and 30%, and the first point on the curves, reflecting the value of the copolymer of MMA with AN, is higher than that of the others. The \bar{M}_w and \bar{M}_n of the PMI–MMA–AN emulsion copolymers decrease with an increasing AN content. This result is similar to that of ref. 2. According to ref. 2, the molecular weight of MMA/PMI/St increases with an increasing PMI feed content (the PMI feed content is lower than 15% in weight) and decreases with an increasing St feed content. In this article, the highest value is in the range of a 15–20% PMI feed content.

For the MMA/PMI/AN copolymerization system, PMI has a higher tendency to copolymerize, so the molecular weight will increase with an increasing PMI feed content. But the molecular

**Figure 2** Relationship of average molecular weight with PMI feed content (batch products).**Figure 3** Relationship of average molecular weight with AN feed content (batch products).

weight is also a function of the termination rate. In emulsion polymerization, termination occurred only when another radical came into the micelles. So, the termination rate was determined by the rate of the radical formation. PMI is easier to form $\text{PMI}\cdot$ than are MMA and AN. This is the reason why the average molecular weight de-

**Figure 4** Relationship of average molecular weight with PMI feed content (semibatch products).

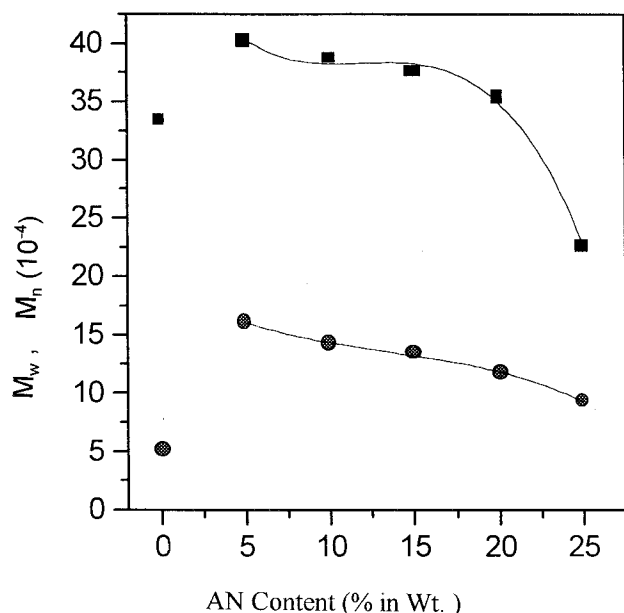


Figure 5 Relationship of average molecular weight with AN feed content (semibatch products).

creases sharply when PMI was introduced into the copolymerization system.

As is known, a polymerization reaction takes place mainly in the 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 v_p and not affected by other effects.⁸ Furthermore, v_p is a function of the monomer feed ratio. If the reactivity ratios are fixed, as reported, it will be maximum at a proper monomer ratio. So, the molecular weight of the copolymer was affected mainly by the monomer feed composition when the copolymerization temperature, emulsifying

agent, and initiator concentrations were fixed and should be maximum at a proper monomer ratio. This is the reason why the average molecular weight of the MMA-PMI-AN emulsion terpolymers varies at different PMI and AN feed contents. It is worth noting that the feed content of PMI, in a constant proportion point of the MMA/PMI copolymerization system, is in the range of 15–20% (in weight),³ and the highest molecular weight of MMA/PMI/AN is also in the same range.

Thermogravimetric Analysis

The thermal stability of the copolymer has been arbitrarily defined as a function of the initial thermal decomposition temperature (T_i) and the half-weight loss temperature (T_{50}) at the particular environmental conditions described previously. Experimental results are given in Tables III and IV. Many studies showed that PMMA is liable to decompose at high temperature. The T_i and T_{50} of PMMA were determined to be 262.4 and 316.6°C, respectively, in our study. The results in Tables III and IV indicate that the thermal stability tends to increase as both the PMI and AN feed contents increase. T_i and T_{50} increased 27.0 and 34.4°C, respectively, when PMMA was copolymerized with 20% PMI and 5% AN (in weight), because of the presence of 1,2-ethylenic units directly linked to MMA units.⁵ The decomposition temperature of the copolymers increases with increasing PMI content, due to the five-member planar ring in the chain. The T_i and T_{50} of PMI-MMA-AN (20 : 55 : 25) are 24.0 and 51.0°C, respectively, higher than those of neat PMMA, and the decomposition temperature also increases with an increasing AN feed content. PAN will take place in the intermolecular reaction at about 200°C, providing six-member rings in the molecular chain.⁹ These chain segments possess a higher decomposition temperature, which will highly restrain the decomposition reaction of PMMA. The sequence length of the AN

Table III T_g , T_{vicat} , and T_{d50} of Copolymers at Different PMI Content (Granule Addition)

Measurement	PMI Content						
	0	5	10	15	20	25	30
T_g (°C)	105.6	117	119	122	126	134	137
T_{d50} (°C)	295.6	334.6	336.1	343.0	351.0	355.0	359.3
T_{vicat} (°C)	104.1	115.8	117.0	115.6	123.4	124.6	126.3

Table IV T_g , T_{vicat} , and T_{d50} of Copolymers at Different AN Content (Granule Addition)

Measurement	PMMA	AN Content					
		0	5	10	15	20	25
T_g (°C)	104.8	138.3	133.3	126.3	126.3	126.3	125
T_{d50} (°C)	316.6	335.0	351.0	357.0	358.5	359.1	367.5
T_{vicat} (°C)	111.9	128.0	123.4	113.7	110.0	109.8	106.1

chain segment will increase while the AN feed content increases. Thus, the incorporation of PMI and AN into MMA in emulsion copolymerization will highly restrain the decomposition reaction of PMMA.

Glass Transition Temperature

The copolymers' T_g was another important indication of their thermal properties. The batch-products' T_g 's determined by TBA are shown in Figures 6 and 7. As seen from Figures 6 and 7, the TBA curves exhibit two T_g 's. This indicates the terpolymers' heterogeneous nature, which is due to the batch emulsion copolymerization. The

higher T_g represents three-composition copolymers that are formed in the earlier stage of the emulsion copolymerization, whereas the lower represents the poly(MMA-co-PMI) chain that formed in the later stage of the emulsion copolymerization. The results show that copolymers' T_g increases with an increasing PMI feed content while decreases with an increasing AN feed content.

It should be noted that the semibatch-product of PMI/MMA/AN(20:75:5) exhibits a single T_g (126°C), while the batch product at same feed composition exhibits two T_g 's (T_{g1} : 99.5°C; T_{g2} : 128°C). The main difference between the batch and semibatch methods is that in the latter, at

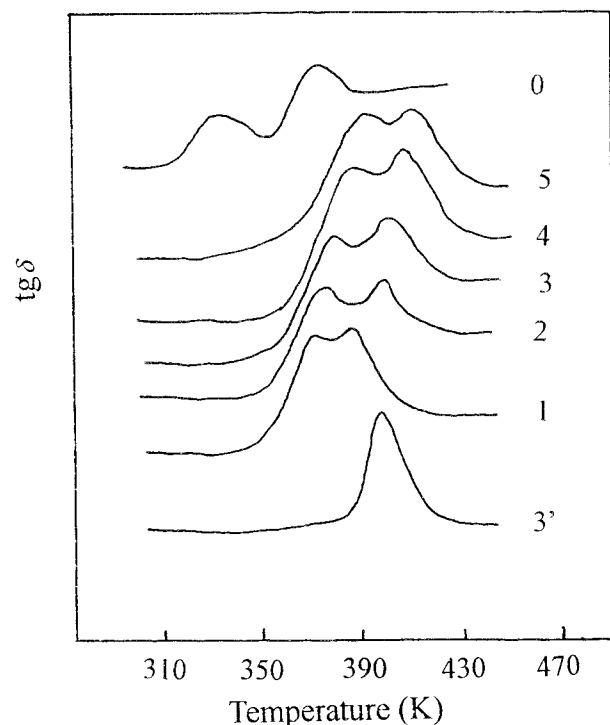


Figure 6 TBA curves of copolymers at different PMI feed content: 0 : 0; 1 : 10; 2 : 15; 3 : 20; 4 : 25; 5 : 30; 3' : 20 (semibatch product).

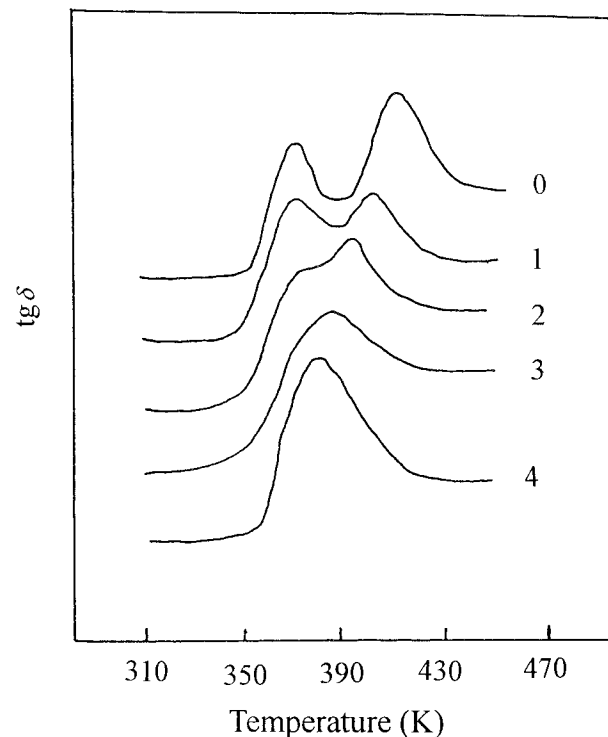


Figure 7 TBA curves of copolymers at different AN feed content: 0 : 0; 1 : 5; 2 : 10; 3 : 15; 4 : 20.

Table V Mechanical Properties of Terpolymers at Different AN Feed Content

Property	AN Feed Content (wt %)						PMMA
	0	5	10	15	20	25	
Impact strength (kJ/m ²)	2.18	1.80	1.94	1.75	1.86	2.23	1.97
Tensile strength (MPa)	35.7	35.3	35.6	39.7	43.0	57.1	36.1

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 . The T_g 's of the semibatch products are summarized in Tables III and IV. As seen from Tables III and IV, the T_g of the semibatch-products increases with an increasing PMI content and decreases slowly with an increasing AN content.

The Vicat softening temperature of the terpolymers are also shown in Tables III and IV. As seen from Table III, the Vicat softening temperature of the terpolymers increases with an increasing PMI feed content. But the Vicat softening temperature of the terpolymers, as seen from Table IV, decreases with an increasing AN feed content.

The glass transition temperature and Vicat softening temperature reflect the stiffness and the movement ability of molecular chain segments. The 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 an increasing PMI feed content. The increasing of the AN feed content will result in the decreasing of the spatial obstruction of internal rotation and the decreasing of the structural stiffness of the molecular chain. This is the reason why the T_g and T_{Vicat} decrease with an increasing AN feed content.

Mechanical Properties

The mechanical properties of the terpolymers at different PMI and AN feed proportions are summarized in Table V and Figures 8 and 9. As seen from Figures 8 and 9, the tensile strength and the impact strength both decrease as the PMI feed content increases from 0 to 30 percent (in weight percent). The PMI-containing terpolymer contains five-member rings in the chain, and this ring contains a big side group (phenyl group), so the interaction of the molecular chain will de-

crease with an increasing PMI content, resulting in a lower tensile strength. The stiffness of the molecular chain increases with an increasing PMI feed content. This is the reason why the impact strength decreases with an increasing PMI feed content. It should be noted that the tensile strength of the terpolymers is higher than that of PMMA when the PMI feed content is lower than 20% (in weight percent).

But the tensile strength of the terpolymers, as seen from Table V, increases with an increasing AN feed content. The tensile strength of poly(PMI-co-MMA), for which the monomer feed composition is 20:80, is 35.7 MPa and increases to 57 MPa when the feed ratio of PMI:MMA:AN is 20:55:25. The molecular entanglement has some influence on the mechanical properties¹⁰: The more entanglement of the terpolymer molecular, the higher are the mechanical properties. The entanglement extent increases with increasing

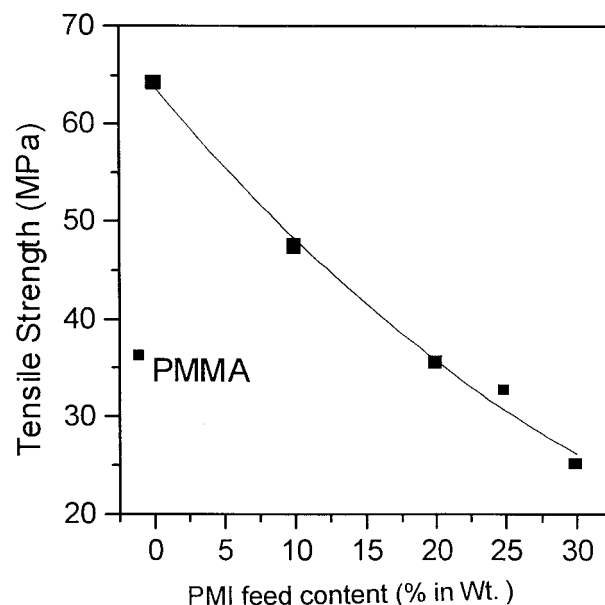


Figure 8 Relationship of tensile strength of the terpolymer with PMI feed content (semibatch products).

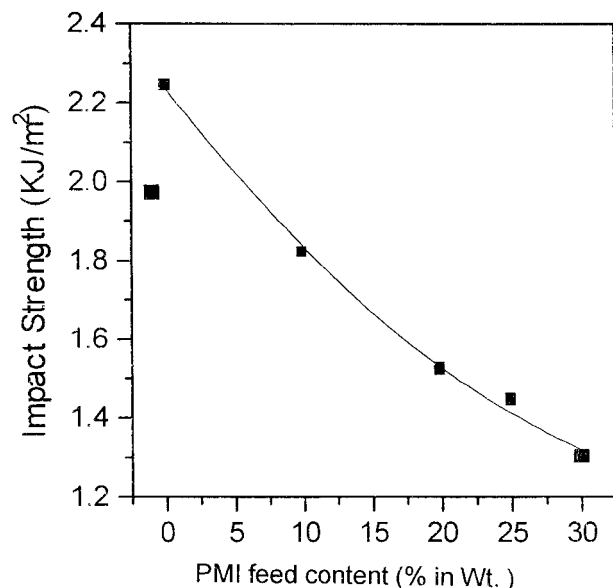


Figure 9 Relationship of impact strength of the terpolymer with PMI feed content (semibatch products).

flexibility of the chain segments. The flexibility will increase with an increasing AN feed content. This is the reason why the mechanical properties of the terpolymers increase with an increasing AN feed content, and the impact strength is in the range of 1.75–2.23 kJ/m². These results show that AN is a useful monomer to improve the mechanical properties of PMI-containing copolymers and is also useful to the thermal properties of the target copolymers.

CONCLUSIONS

According to our experimental results, four points can be concluded as follows:

1. Semibatch emulsion copolymerization of PMI, MMA, and AN produces copolymers

- with a homogeneous chain structure, as evidenced by their single T_g .
2. The composition of semibatch copolymers is almost the same as that of the feed composition.
3. PMI is an effective monomer for improving the thermal properties of PMMA, especially the glass transition temperature, decomposition temperature, and Vicat softening temperature.
4. The AN chain segment is useful to the mechanical properties of poly(MMA-co-PMI). The suitable content should be in the range of 10–15%.

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