

Self-Compatibilization of Poly(butyl methacrylate)/Acrylonitrile-co-Styrene Blends via Concentrated Emulsion Polymerization

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SYNOPSIS

Two concentrated emulsions in water were prepared: one from weakly polymerized butyl methacrylate (BMA) and the other one from a weakly polymerized mixture of acrylonitrile (AN) and styrene (St). Each of the concentrated emulsions also contained a small amount of a vinyl-terminated macromonomer (VTM). After the concentrated emulsions were partially polymerized, they were mixed and subjected to complete polymerization. This generated a blend of poly(butyl methacrylate) (PBMA), binary copolymer AN-co-St (AN-St), and networks containing chains of VTM and those formed from different monomers. The networks constitute compatibilizers between the PBMA and AN-St. Such a preparation method, in which the components and compatibilizer are generated simultaneously, was called self-compatibilization. The blend possesses excellent tensile properties and toughness compared with the ternary copolymer AN-St-BMA and with the solution blends of PBMA/AN-St. The generation of the compatibilizers and the compatibilization mechanism were investigated via kinetic studies. The effects of the VTM, polymerization conditions, and the weight ratio of AN/St were also examined. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

New polymeric materials can be developed by combining monomers and/or polymers with different chemical structures via copolymerization, grafting, or blending. For a random copolymer, the mechanical properties are usually near or below the weight average of the individual homopolymers. In contrast, for a polymer blend, each constituent may retain some of the features of its own structure, but, most important, a synergism in mechanical properties can be achieved.^{1,2} For instance, a stiff component can be toughened via its blending with flexible components.^{3,4} However, in the preparation of a blend from incompatible polymers, the problem of incompatibility may arise and, as a result, the mechanical properties of the blend may catastrophically fall be-

low those of the homopolymers. A large number of attempts were made to improve the compatibility of blends, either by generating specific interactions or chemical reactions between different components, or via the addition of a compatibilizer.⁵⁻⁷ The preparation and compatibilization of polymer blends were mostly achieved by melt mixing, usually in an extruder.^{8,9} However, if special functional groups are absent in the components, no specific interactions or chemical reactions can occur. The preparation of compatibilizers, usually diblock copolymers, is, in general, sophisticated and expensive.

For these reasons, an alternative approach to the formation and compatibilization of blends of immiscible polymers—namely, self-compatibilization¹⁰ via concentrated emulsion polymerization^{11,12}—was developed by this group. In this approach, two concentrated emulsions (A and B) of different monomers in water, each monomer also containing a small amount of vinyl-terminated macromonomer (VTM), were prepared and subjected to partial polymerization. A concentrated emulsion¹³⁻¹⁵ has the appear-

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ance of a paste and differs from the conventional emulsion in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of spheres of the same size) and may be as high as 0.99. At high volume fractions, the concentrated emulsions contain polyhedral cells separated by thin films of continuous phase. A blend was obtained by mixing the partially polymerized concentrated emulsions and subjecting the mixture to complete polymerization. Both before and after the two concentrated emulsions were mixed, networks were formed via the reactions between the VTM and the monomers. Before the concentrated emulsions were mixed, the network contained chains of VTM and those formed from the corresponding monomer. After the concentrated emulsions were mixed, the networks could also include chains of the other kind of monomer as well as copolymer chains of all monomers. Because of the affinity among the VTM chains of different networks and the affinity among the homo- and/or copolymer chains present outside and as constituents of the networks, the networks constitute good compatibilizers for the system. A distinctive feature of this method is that the polymers which are blended and the compatibilizers are generated simultaneously. In other words, a compatibilized blend is produced via a single complete polymerization. Since the formation of the network occurs independently in each latex particle, the crosslinking is limited to each latex, and the latexes have flowability.

In the self-compatibilization, the transfer of the monomers among the cells of the two concentrated emulsions must be controlled. If the transfer is too advanced, the product will be a copolymer of all the monomers and not a blend. The monomer transfer can be easily controlled by changing the viscosity of the system.

In a previous article,¹⁰ blends of styrene-*co*-methyl methacrylate and poly(vinyl acetate) were compatibilized via vinyl-terminated polycaprolactone (VTPCL) using the concentrated emulsion polymerization. The VTPCL was introduced in the concentrated emulsions because it generates networks which compatibilize the system. The copolymerizations between styrene (St) and vinyl acetate and between methyl methacrylate and vinyl acetate occur with difficulty, and hence only a small amount of ternary copolymer is generated. For this reason, the initial partial polymerization can be avoided in this case. It is also important to note that even if a random ternary copolymer had been formed, short

sequences of each of the monomers could not compatibilize the system. In the present article, blends of the polar acrylonitrile-*co*-styrene (AN-St) and nonpolar poly(butyl methacrylate) (PBMA) were investigated. Changing the ratio of acrylonitrile (AN) to styrene, the extent of polarity of AN-St can be significantly varied. Such systems were employed to demonstrate the broad applicability of the self-compatibility procedure based on concentrated emulsions. In addition, AN, styrene, and butyl methacrylate (BMA) can form without difficulty a ternary copolymer. Consequently, the control of the transfer of the monomers becomes important. It is shown in this article that, in an AN-St-BMA ternary copolymer, no toughening by BMA can be achieved, whereas in a self-compatibilized AN-St/PBMA blend, prepared via concentrated emulsions, a strong toughening of AN-St by PBMA can occur. The extent of toughening is used in this article as a measure of compatibilization.

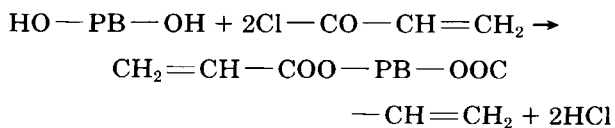
MATERIALS AND METHODS

Materials

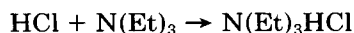
Azobisisobutyronitrile (AIBN, Kodak) was recrystallized from methanol. All the other chemicals were purchased from Aldrich. St, BMA, and AN were filtered through an inhibitor removal column before use. The other compounds, polycaprolactone diol (PCL diol, *MW* 2000), poly(butadiene) diol (PB diol, *MW* 2800), triethylamine (TEA, 99%), acryloyl chloride (AC, 96%), sodium dodecyl sulfate (SDS, 70%), toluene (99%), tetrahydrofuran (THF, 99%), and dimethyl formamide (DMF, 99%) were used as received.

Preparation of the VTMs

A solution of PB diol or PCL diol in toluene (20 g per 100 mL) was introduced in a single-necked flask equipped with a magnetic stirring bar. TEA (1 mole for each mole of OH groups of the dissolved diol) was added to the solution, and the flask was sealed with a rubber septum. AC (1 mole for each mole of OH groups) was introduced dropwise with stirring with a syringe through the rubber septum, at room temperature. The OH group reacts with AC to form a vinyl group:



The HCl molecules produced in the preceding reaction react with TEA:



and the formed quaternary ammonium salt remains suspended in the system as a white powder. Removing the white powder by filtering, a toluene solution of vinyl-terminated PB or PCL was obtained, which was subsequently used at a concentration of 0.2 g/mL.

Preparation of the Concentrated Emulsion Blends

BMA or a mixture of AN and styrene containing an initiator (AIBN, 0.005 g/g monomers) was partially polymerized at 50°C for 1 h in order to increase the viscosity moderately. (A too high viscosity impedes the generation of a concentrated emulsion, while a too low viscosity makes the concentrated emulsion unstable during its heating at high temperatures.) The VTM solution can be introduced into the monomers before or after their partial polymerization, or even later, after the mixing of the two concentrated emulsions. The two partially polymerized systems were subsequently used as the dispersed phases of two concentrated emulsions. In the preparation of a concentrated emulsion, an aqueous solution of SDS (10 wt %) was first placed in a flask provided with a magnetic stirrer. The flask was sealed with a rubber septum, after which the air inside was replaced with nitrogen. The partially polymerized monomer was added dropwise with vigorous stirring into the flask with a syringe, until the volume fraction of the SDS aqueous solution became 0.2. The whole addition process lasted about 15 min and took place at room temperature. The two concentrated emulsions thus prepared were introduced into a water bath at 50°C to carry out another partial polymerization for a selected time span. Subsequently, the two concentrated emulsions were mixed, and the mixture was further heated at 50°C for 48 h for completing the polymerization. In the kinetic study, the final polymerization lasted between 0 and 48 h. The product obtained was washed with methyl alcohol and dried in a vacuum oven for 24 h. The blend product of the concentrated emulsion polymerization was obtained as a white powder, and the ratio of the weight of the powder to the original weight of the reactants was considered as the conversion.

Preparation of Solution Blends and Copolymers

Solution blends were obtained by casting solutions of AN–St and PBMA in DMF on glass plates and evaporating the solvent. Binary copolymers of AN–St and ternary copolymers of AN–St–BMA were prepared by bulk polymerization at 50°C for 24 h.

The Tensile Testing

The powders of the concentrated emulsion blends or the bulk materials of the solution blends or copolymers were thermopressed with a Laboratory Press (Fred S. Carver Inc.) at 150°C for 3–5 min and then cooled to room temperature. The sheets thus obtained were cut with a die to the size required by ASTM D.638. The tensile testing was conducted at room temperature, with an Instron Universal Testing Instrument (Model 1000). The elongation speed of the instrument was 20 mm/min.

Solubility Measurements

The solubility measurements of the concentrated emulsion blends were conducted in a sequential way. A preweighed blend sheet prepared as for tensile testing was immersed in toluene in a test tube at room temperature, using 10 mL of solvent for each gram of sheet. The solvent in the tube was changed with a fresh one each 8 h, until all the soluble species had been removed (less than 48 h). The remaining sheet was dried in a vacuum oven for 24 h to remove the solvent. The ratio of the weight lost to that of the original sheet was denoted as toluene removed fraction (in wt %). The remaining sample was further immersed in THF at 50°C and finally in DMF at 50°C. The ratios of the weight lost in the THF or DMF to that of the original sheet are denoted as THF or DMF removed fractions (in wt %), respectively. The weight ratio of the final remaining sample to the original sheet was considered as the network content (the crosslinked part of the blend, in wt %).

RESULTS AND DISCUSSION

Solution Blends

A series of AN–St/PBMA blends was prepared via solution blending. For the AN–St copolymers, the weight ratios of AN and St were 0/100, 25/75, 50/50, and 75/25, respectively. The weight ratio of AN–St/PBMA was 1/1. The incompatibility of these blends can be predicted from the chemical structures

as well as the solubility parameters of the two polymers. The solubility parameters of polyacrylonitrile (PAN), polystyrene (PS), and PBMA are 31.5,¹⁶ 17.8,¹⁷ and 14.7¹⁸ (MPa)^{1/2}, respectively. The difference between the values of these parameters for PS and PBMA is large enough for them to be incompatible; the difference for PBMA and AN-St is even larger. Regarding the chemical structures, the flexible butoxy groups are quite different from the bulky phenyl groups of PS or from the strong polar CN groups of PAN. Indeed, the incompatibility of AN-St/PBMA solution blends was revealed by the non-uniformity of the materials obtained. Phase separation could be detected with the naked eye. The toughnesses of the blends, expressed as the areas under the stress-strain curves, were extremely low, in the range of 3–5 MJ/m³; the elongations at break were below 10%. It is obvious that such blends, without compatibilization, can hardly be useful in any application.

Copolymers

The mechanical properties and solubilities are listed in Table I, which, for comparison purposes, also contains the properties of BMA homopolymers. One can see that the mechanical properties of the ternary copolymers are essentially the weight averages of those of AN-St and PBMA. As mentioned in the "Introduction," since the different units are randomly distributed, no toughening of AN-St by PBMA can be achieved. Even when the BMA fraction is higher than 50 wt %, the toughness is still very low. The solubility measurements of the copolymers in the three solvents (toluene, THF, and DMF) were carried out separately and not sequen-

tially, as they have been carried out for the concentrated emulsion blends. The results show that the solubilities in various solvents can be roughly evaluated on the basis of the content of AN, which determines the polarity of the copolymer. Toluene dissolves the copolymers with an AN content below 10 wt % and partially dissolves those with an AN content between 10 and 25 wt %. THF dissolves the copolymers with an AN content up to 25 wt % and partially dissolves those with an AN content between 25 and 33 wt %. All the copolymers dissolve completely in DMF. The foregoing results have suggested the solubility measurement procedure, presented in "Materials and Methods," which can be used to obtain qualitative information about the composition of the concentrated emulsion blends.

Kinetic Studies

Overall Conversions

Kinetic studies were carried out on six systems which lead to concentrated emulsion blends. The overall conversion, composition, and mechanical properties of the products at different times are presented in Tables II–VII, which also provide detailed information about the systems involved. In all these systems, conversions above 89 wt % can be reached within 24 h. Comparing Tables II, III, and IV, one can see that an increase in AN decreases somewhat the initial polymerization rate. For the same polymerization time, the system with a lower AN content has a higher conversion. However, after 24 h, the conversions of the three systems are nearly the same. A comparison between any of the Tables II, III, and IV with Table VII indicates that the presence of

Table I Properties of the Copolymers

Composition		Solubility		Mechanical Properties			
		Toluene Soluble (Wt %)	THF Soluble (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
Weight Ratio AN/St/BMA	AN (Wt %)						
75/25/0	75	0	0		Too brittle to be measured		
50/50/0	50	0	0	84.1	8	1800	6.3
33/33/33	33	0	50	62.5	16	1230	7.3
25/75/0	25	18	100	81.0	7	1505	4.9
25/25/50	25	20	100	52.0	8	1060	4.7
17/17/66	17	26	100	41.7	23	910	5.5
10/10/80	10	100	100	32.8	73	480	20.4
0/0/100	0	100	100	20.5	150	305	20.4

Table II Kinetic Data for the Concentrated Emulsion Blend No. 1

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)				Mechanical Properties and (Standard Error)			
		Toluene Removed	THF Removed	DMF Removed	Network Content	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
		0	9.2	55.3 (5.1)	35.0 (3.2)	0	9.7 (0.9)	17.3 (0.5)	35 (1.0)
3	39.8	39.6 (15.7)	25.3 (10.1)	0	35.1 (14.0)	28.3 (1.5)	91 (4.9)	524 (38)	20.8 (1.7)
6	71.1	42.6 (30.3)	29.3 (20.9)	0	28.1 (20.0)	33.6 (1.9)	114 (1.8)	630 (14)	30.4 (2.7)
12	89.2	43.9 (39.2)	33.4 (29.8)	0	22.6 (20.2)	36.0 (2.8)	83 (6.0)	676 (12)	25.1 (1.8)
24	94.0	42.1 (39.6)	36.2 (34.0)	0	21.7 (20.4)	38.1 (2.7)	81 (3.1)	720 (28)	26.1 (2.7)
48	98.0	40.9 (40.1)	37.9 (37.2)	0	21.1 (20.6)	39.5 (1.9)	75 (4.2)	724 (32)	25.9 (0.8)

Weight ratio of AN/St = 25/75, weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt % in monomer system. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min.

VTM also decreases the initial polymerization rate. However, the conversions after 24 h are not affected.

Conversion and Composition

The concentrated emulsion polymerization leading to a blend constitutes a very complicated process since several reactions take place simultaneously. Before the two concentrated emulsions are mixed, the homopolymerization of BMA, the copolymerization of AN and St, and the network formation between VTM and the monomers take place. After the concentrated emulsions are mixed, ternary copolymerization and a large variety of networks are, in addition, generated. Hence four kinds of polymers—PBMA, binary copolymer AN–St, ternary copolymer AN–St–BMA, and networks—are present in a concentrated emulsion blend. It is almost impossible to determine its exact composition. On the basis of the solubility measurements described in “Materials and Methods,” the species in such a blend can be divided in four groups: PBMA and copolymers with an AN content below 10 wt %, which are completely soluble in all three solvents; copolymers with an AN content between 10 and 33 wt %, which are completely soluble in THF and DMF; copolymers with an AN content above 33 wt %, which are completely soluble in DMF; and network species. In a first approximation we will consider that the four groups of species identified by the solubility measurements roughly represent the four types of polymers present in the system.

From the solubility data of Tables II–VII, one can see that, in the final products, the content of the crosslinked structure is between 20 and 25 wt

%; the content of the ternary copolymer is below 6 wt %; and the content of BMA homopolymer and binary copolymer AN–St is higher than 70 wt %. The rates of formation of various components are different. The network structure is mostly formed before a conversion of 50 wt %; above 50 wt % conversion, the increase in network content is negligible. This indicates that, in spite of its longer length, the VTM possesses a higher reactivity than the monomers, which are smaller. It also indicates that the polymers formed after 50 wt % conversion are mostly the linear ones. This explains why the network acts as a compatibilizer; once a linear polymer chain is formed, it will tend to locate near a network chain of similar chemical structure. Consequently, the various parts of the network are in contact with different linear chains and the compatibilization is achieved.

Conversion and Mechanical Properties

One may observe that the samples on the first rows of Tables II, III, IV, and VI, for which the conversion is low, possess very poor mechanical properties. Since those samples were obtained immediately after the two concentrated emulsions were mixed, the network content is very low, since most of VTM has not yet reacted. Consequently, the mechanical properties are poor. The yield strength and Young's modulus increase as the conversion increases. This can be related to the content of AN–St, which has a high yield strength and a high Young's modulus. The AN–St content (represented by the wt % of DMF removed species in Tables III–VI) exhibits a minimum, after which it increases as the conversion

Table III Kinetic Data for the Concentrated Emulsion Blend No. 2

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)				Mechanical Properties and (Standard Error)			
		Toluene Removed	THF Removed	DMF Removed	Network Content	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	8.5	50.5 (4.2)	0 (0)	35.8 (3.0)	12.9 (1.1)	19.9 (0.2)	15 (0.7)	271 (10)	2.4 (0.2)
3	29.8	24.3 (7.2)	5.7 (1.7)	38.2 (11.4)	31.8 (9.5)	25.7 (2.8)	66 (2.6)	598 (27)	13.8 (0.7)
6	64.2	33.1 (21.3)	4.6 (3.0)	26.1 (11.8)	36.1 (23.1)	33.0 (1.1)	154 (6.3)	631 (21)	42.7 (1.7)
12	73.4	43.2 (31.7)	5.2 (3.7)	28.3 (20.8)	31.9 (23.4)	37.2 (0.8)	125 (5.2)	693 (12)	38.6 (1.1)
24	93.5	41.3 (38.6)	5.2 (4.9)	28.0 (26.2)	25.5 (23.8)	39.1 (1.4)	118 (8.4)	796 (12)	38.7 (2.1)
48	100	39.2 (39.2)	5.5 (5.5)	31.8 (31.8)	24.2 (24.2)	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt % in monomer system. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min.

increases. This indicates that the monomers AN and styrene are mainly consumed in the formation of networks in the early stages of polymerization. After the network formation is nearly completed, they form mainly linear AN–St copolymer. However, both the network chains and the linear chains of AN–St provide a similar contribution to the yield strength and Young's modulus: the higher the content of AN–St chains, the higher the yield strength and Young's modulus. The elongation at break and the toughness exhibit a maximum around a conversion of 40–60 wt %. They can be related to the relative proportion of flexible chains (i.e., PBMA and VTM chains). As mentioned before, the VTM molecules are mostly included in the network before a conversion of 50 wt % is achieved. In addition, one

can note that the toluene removed species increases little after a conversion of about 90 wt %, which indicates that BMA was nearly consumed at that conversion. Consequently, the chains formed after a conversion of 90 wt % are mainly those of the AN–St copolymer. The different rates of formation of different species result in a maximum content of flexible chains at a conversion of 40–60 wt %. As a result, maxima of the elongation at break and the toughness occur.

Effect of VTM

Content of VTM

VTM is the key precursor of the network compatibilizer. Without VTM, the products will con-

Table IV Kinetic Data for the Concentrated Emulsion Blend No. 3

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)				Mechanical Properties and (Standard Error)			
		Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	7.8	56.5 (4.4)	0	28.2 (2.2)	8.4 (0.7)	20.6 (0.8)	30 (1.5)	301 (10)	4.9 (0.8)
3	30.0	45.7 (13.7)	3.4 (1.0)	20.4 (6.1)	30.5 (9.2)	33.1 (1.8)	147 (1.0)	624 (32)	41.3 (1.8)
6	53.9	37.1 (20.0)	3.0 (1.6)	21.3 (11.5)	38.6 (20.8)	37.9 (1.0)	120 (3.4)	684 (15)	37.2 (3.5)
12	75.0	39.8 (29.9)	3.6 (2.7)	28.4 (21.3)	28.2 (21.2)	40.6 (1.8)	104 (1.7)	733 (28)	34.6 (3.0)
24	89.7	41.6 (37.3)	3.6 (3.2)	30.9 (27.7)	23.9 (21.4)	42.4 (1.6)	95 (2.8)	784 (16)	33.5 (2.7)
48	95.2	40.5 (38.6)	3.3 (3.1)	33.5 (31.9)	22.7 (21.6)	47.0 (1.3)	82 (6.3)	822 (34)	32.0 (1.5)

Weight ratio of AN/St = 75/25, weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt % in monomer system. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsion before mixing: 30 min.

Table V Kinetic Data for the Concentrated Emulsion Blend No. 4

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)				Mechanical Properties and (Standard Error)			
		Toluene Removed	THF Removed	DMF Removed	Network Content	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	32.0	39.1 (12.5)	0	23.1 (7.4)	37.8 (12.1)	14.8 (0.6)	82 (3.7)	304 (10)	9.6 (0.8)
3	52.5	35.2 (18.4)	0.9 (0.5)	20.0 (10.5)	43.8 (23.0)	18.6 (1.9)	105 (4.5)	374 (32)	16.6 (0.9)
6	63.8	39.8 (25.4)	1.1 (0.7)	22.5 (14.4)	36.5 (23.3)	20.9 (1.7)	94 (2.7)	432 (10)	16.5 (1.3)
12	79.9	39.9 (30.0)	1.4 (1.1)	26.9 (20.1)	31.8 (23.8)	26.5 (1.2)	81 (1.3)	484 (16)	17.4 (1.6)
24	95.3	39.6 (37.7)	1.7 (1.6)	33.4 (31.8)	25.3 (24.1)	28.8 (1.5)	68 (2.0)	515 (5)	16.2 (1.3)
48	98.9	39.4 (38.0)	1.8 (1.8)	35.1 (34.7)	24.6 (24.3)	30.9 (1.2)	58 (2.5)	594 (4)	15.2 (0.7)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt % in monomer system. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 2 h.

sist of a mixture of a homopolymer and binary and ternary copolymers with poor compatibility; their toughness and elongation at break are very low, as one can see by comparing Table III with VII and Table VIII with IX. The toughness of the samples containing 5 wt % VTM is three to five times higher than that of those free of VTM. However, because of the presence of the soft chains of VTM, the yield strength and Young's modulus are somewhat lower than of those without VTM. The effect of VTM content can be seen from Table X, in which the VTPCL content changes from 0 to 10 wt %. There is an abrupt increase in the elongation at break and toughness from the sample

containing 2.5 wt % to that containing 5 wt % VTPCL. This indicates that 2.5 wt % VTPCL is not enough to achieve a good compatibilization. When the VTPCL content increases from 5 wt % to 10 wt %, the toughness increases only a little but the yield strength and Young's modulus decrease, because larger amounts of soft chains are introduced. One can conclude that a VTPCL content of 5 wt % provides the optimum benefit.

Addition Procedure

Not only the amount of VTPCL introduced, but also the moment of its addition, affects the compatibil-

Table VI Kinetic Data for the Concentrated Emulsion Blend No. 5

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)				Mechanical Properties and (Standard Error)			
		Toluene Removed	THF Removed	DMF Removed	Network Content	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	15.8	52.4 (8.3)	0	36.8 (5.8)	10.8 (1.7)	4.8 (0.6)	57 (0.7)	150 (2)	2.2 (0.2)
3	37.8	25.2 (9.5)	2.1 (0.8)	17.7 (6.7)	36.0 (13.6)	28.9 (1.2)	74 (7.0)	448 (6)	17.3 (0.8)
6	67.9	37.2 (25.3)	5.2 (3.5)	29.3 (19.9)	28.3 (19.2)	30.8 (0.7)	161 (5.2)	531 (11)	42.1 (3.6)
12	84.4	39.6 (33.4)	5.4 (4.6)	31.4 (26.5)	23.6 (19.9)	32.8 (1.1)	153 (7.0)	619 (27)	41.4 (3.7)
24	90.3	39.6 (35.8)	5.8 (5.2)	32.3 (29.2)	22.3 (20.1)	37.2 (2.5)	144 (6.3)	637 (59)	42.8 (2.6)
48	100	36.3 (36.3)	5.9 (5.9)	37.4 (37.4)	20.4 (20.4)	38.9 (1.2)	132 (13)	642 (41)	40.6 (1.5)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1, VTPB = 5 wt % in monomer system. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min.

Table VII Kinetic Data for the Concentrated Emulsion Blend No. 6

Time of Polymn. after the Concentrated Emulsions Were Mixed (h)	Conversion (Wt %)	Solubilities: Wt % in Product and (Wt % of the Initial Reactants)			Mechanical Properties and (Standard Error)			
		Toluene Removed	THF Removed	DMF Removed	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	8.6	64.0 (5.5)	0	36.0 (3.1)	22.6 (1.3)	26 (1.2)	215 (9)	4.7 (0.3)
3	57.7	59.0 (34.0)	8.0 (4.6)	33.0 (19.0)	33.8 (2.3)	39 (1.4)	675 (53)	10.7 (1.1)
6	88.5	56.0 (49.6)	7.5 (6.6)	36.5 (32.3)	45.8 (1.9)	62 (2.9)	778 (15)	23.6 (1.8)
12	91.3	54.8 (50.0)	7.6 (6.9)	37.5 (34.2)	47.4 (0.7)	45 (1.7)	823 (42)	17.3 (1.3)
24	93.6	53.7 (50.3)	8.7 (8.1)	37.6 (35.2)	52.5 (2.1)	35 (2.1)	899 (38)	14.7 (1.2)
48	96.3	52.8 (50.8)	9.0 (8.7)	38.2 (36.8)	53.1 (1.7)	24 (1.7)	912 (21)	6.1 (0.7)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1, no VTM introduced. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min.

ization. The results of the various addition procedures of VTPCL are presented in Table XI. Five procedures were employed: (1) VTPCL was partially polymerized with the monomer(s) from the beginning; (2) VTPCL was introduced after the partial polymerization of the monomer(s), before the preparation of the concentrated emulsion; (3) VTPCL was introduced into the mixed concentrated emulsions; (4) a third concentrated emulsion of VTPCL solution in water was prepared and mixed with the other two concentrated emulsions; and (5) the same as procedure 2, but the partial polymerization of each concentrated emulsion lasted 2 h before they were mixed. One can see that procedures 1 and 5 provide lower mechanical properties. The reason is that the VTPCL reacted for too long with the monomers of only one concentrated emulsion. As a result, the

compatibilizing effect was poor. Comparable mechanical properties were obtained via procedures 2-4. This indicates that only when the VTM has enough time to react with the monomers of both concentrated emulsions can good compatibilization be achieved.

Comparison of Different VTMs

Vinyl-terminated polybutadiene (VTPB) was also employed in the self-compatibilization of AN-St and PBMA. The data based on VTPB and VTPCL are presented in Table XII as well as in Tables III and VI. Since the molecular weight of VTPB employed is higher than that of VTPCL (2800 vs. 2000), the number of VTPB molecules is lower for the same weight fraction. For this reason, the net-

Table VIII Comparison of Various AN/St Weight Ratios

AN/St Weight Ratio	Solubilities			Mechanical Properties and (Standard Error)			
	Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0/100	100	0	0	50.9 (1.2)	17 (1.0)	889 (25)	7.1 (0.2)
25/75	54.6	45.4	0	51.0 (4.0)	17 (1.6)	904 (15)	7.1 (0.6)
50/50	52.5	9.0	38.5	53.1 (1.7)	24 (1.7)	912 (21)	10.6 (0.7)
66/33	44.3	5.5	50.2	53.5 (1.4)	33 (1.3)	914 (45)	15.1 (0.8)
75/25	40.8	4.3	54.9	54.2 (0.7)	19 (1.5)	927 (60)	8.7 (0.8)

Weight ratio of (AN + St)/BMA = 1/1, no VTM introduced. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min. Time of polymerization of the mixture of concentrated emulsions: 48 h.

Table IX Comparison of Various AN/St Weight Ratios

AN/St Weight Ratio	Solubilities				Mechanical Properties and (Standard Error)			
	Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0/100	80.6	0	0	19.4	37.4 (1.3)	58 (3.0)	715 (35)	18.2 (0.4)
25/75	40.9	37.9	0	21.1	39.5 (1.9)	75 (4.2)	724 (32)	25.9 (0.8)
33/66	41.7	31.3	5.6	21.4	40.3 (0.5)	96 (3.7)	736 (8)	31.7 (1.5)
50/50	39.2	5.5	31.8	24.2	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)
66/33	41.2	3.8	30.9	24.1	44.1 (1.7)	119 (8.8)	791 (33)	43.5 (2.7)
75/25	40.5	3.3	33.5	22.7	47.0 (1.3)	82 (6.3)	822 (34)	32.0 (1.5)

Weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt %. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min. Time of polymerization of the mixture of concentrated emulsions: 48 h.

work content of the VTPB-based samples is also lower. In addition, because the PB chains are longer and more flexible than the PCL chains, the VTPB-based samples possess higher elongation at break and toughness and lower yield strength and Young's modulus.

Control of the Monomer Transfer

When two concentrated emulsions are mixed with stirring, the transfer of monomers among the cells cannot be avoided. However, only a suitable transfer of the monomers is effective for self-compatibilization. If the monomer transfer is too advanced, the product will be a ternary copolymer instead of a blend. To avoid the undesired copolymerization, the monomer transfer must be controlled by increasing the viscosity of the concentrated emulsions before they are mixed, by partial polymerization. The effect of the monomer conversion in the partial

polymerization is presented in Table XIII. One can see that if the conversions are lower than 9.9 wt % for BMA and 7.2 wt % for the mixture of AN and St, respectively, the final product has a high THF removed wt %, which indicates a high content of ternary copolymers. As a result, the toughness is low. As the conversions (viscosities as well) of the concentrated emulsions which are mixed increase, the content of ternary copolymer decreases (indicated by the THF removed wt %) and the toughnesses are much better. On the other hand, the partial polymerization of each concentrated emulsion should not be too advanced. The fifth row of Table XIII shows that when each of the concentrated emulsions reaches a very high conversion before their mixing, a low toughness is obtained. This happens because almost all the VTM reacts with the monomers of only one of the concentrated emulsions; as a result, the compatibilization is poor. A comparison of Tables III and V leads to the same

Table X Comparison of Various VTPCL Contents

Fraction of VTPCL (Wt %)	Solubilities				Mechanical Properties and (Standard Error)			
	Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0	52.5	9.0	38.5	0	53.1 (1.7)	14 (1.7)	912 (21)	6.1 (0.7)
2.5	49.2	6.2	33.7	11.2	50.3 (2.5)	25 (2.5)	875 (63)	10.5 (1.5)
5.0	39.2	5.5	31.8	24.2	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)
10.0	29.5	4.2	24.8	41.5	35.7 (1.7)	159 (13)	678 (11)	40.5 (2.1)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min. Time of polymerization of the mixture of concentrated emulsions: 48 h.

Table XI Comparison of Different Addition Procedures of the VTM

No. of VTPCL Addition Procedure	Solubilities				Mechanical Properties and (Standard Error)			
	Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
1	35.2	3.9	31.3	29.6	35.0 (0.8)	39 (3.6)	622 (10)	11.4 (1.2)
2	39.2	5.5	31.8	24.2	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)
3	37.5	5.7	30.4	26.4	39.5 (0.7)	112 (3.3)	747 (29)	36.7 (1.4)
4	36.2	4.9	33.1	25.8	43.3 (1.7)	124 (6.3)	778 (17)	45.6 (2.2)
5	39.4	1.8	35.1	24.6	30.9 (1.2)	58 (2.5)	594 (4)	15.2 (0.7)

Weight ratio of AN/St = 50/50, wt ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt %. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing was 30 min for rows 1–4, 2 h for row 5. Time of polymerization of the mixture of concentrated emulsions: 48 h.

conclusion. The highest conversions for which the two concentrated emulsions can be mixed uniformly are presented in the fifth row of Table XIII. Beyond those conversions, the concentrated emulsions acquire a too high viscosity and the uniform mixing becomes impossible.

The Effect of AN/St Ratio

The AN/St weight ratio in the concentrated emulsions containing AN and St was varied between 0/100 and 75/25. Since AN is very polar, it cannot be used alone to prepare a concentrated emulsion in water; it can, however, be used together with a more hydrophobic monomer such as styrene. The effect of the AN/St weight ratio on the final self-compatibilized blend with PBMA can be found in

Tables VIII, IX, and XIV. The higher the AN content, the higher the yield strength and Young's modulus, because of the strong attraction between the polar CN groups. It is interesting to note that both the elongation at break and the toughness exhibit a maximum. The main obstacle to elongation is caused by the phenyl groups. The higher the AN/St weight ratio, the lower the phenyl group density and hence the longer the elongation at break. However, if the AN/St weight ratio becomes too high, the intermolecular forces between the polar CN groups become dominant and the elongation at break decreases. The presence of AN among the styrene units increases the flexibility as long as the content of AN is not too large. When the content of AN is large, the interaction forces between the polar CN groups decrease the flexibility. For

Table XII Comparison of Different VTMs

AN/St Weight Ratio	VTM (Wt %)	Mechanical Properties and (Standard Error)			
		Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
25/75	PCL5%	39.5 (1.9)	75 (4.2)	724 (32)	25.9 (0.8)
25/75	PB5%	36.7 (2.5)	104 (5.2)	626 (30)	31.5 (2.8)
50/50	PCL5%	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)
50/50	PB5%	38.9 (1.2)	132 (13)	642 (41)	40.6 (1.5)
75/25	PCL5%	47.0 (1.3)	82 (6.3)	822 (34)	32.0 (1.5)
75/25	PB5%	40.3 (1.9)	111 (3.5)	704 (29)	37.7 (2.2)
50/50	PCL10%	35.7 (1.7)	159 (13)	678 (11)	40.5 (2.1)
50/50	PB10%	35.8 (1.7)	168 (9)	603 (27)	50.6 (3.7)

Weight ratio of (AN + St)/BMA = 1/1. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min. Time of polymerization of the mixture of concentrated emulsions: 48 h.

Table XIII Comparison of Various Times of Partial Polymerization of the Concentrated Emulsions

Time of Polymn. before the Concentrated Emulsions Were Mixed (h)	Conversion* (Wt %)		Solubilities				Mechanical Properties and (Standard Error)			
			Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
	BMA	AN/St								
0	7.1	4.9	32.1	17.8	25.2	24.9	28.9 (1.0)	39 (3.6)	607 (32)	9.7 (0.7)
0.5	9.9	7.2	39.2	5.5	31.8	24.2	42.0 (1.3)	115 (9.1)	766 (35)	37.5 (0.8)
1.0	14.8	9.9	37.6	4.6	30.7	27.1	41.5 (2.7)	123 (6.0)	767 (28)	40.8 (4.2)
1.5	26.8	16.6	38.1	4.0	33.9	24.0	38.9 (1.0)	93 (1.5)	689 (6)	30.5 (1.5)
2.0	36.0	22.0	39.4	1.8	35.1	24.6	30.9 (1.2)	58 (2.5)	594 (4)	15.2 (0.7)

Weight ratio of AN/St = 50/50, weight ratio of (AN + St)/BMA = 1/1, VTPCL = 5 wt %. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of polymerization of the mixture of concentrated emulsions: 48 h.

* Partial conversion in each concentrated emulsions before they were mixed.

this reason, the toughness passes through a maximum. One can see from Tables VIII, IX, and XIV that the optimum AN/St weight ratio is located between 50/50 and 66/33.

As already mentioned, the solubility parameters of PAN, PS, and PBMA are 31.5, 17.8, and 14.7 (MPa)^{1/2}, respectively. Assuming a linear additivity for the solubility parameter of a random copolymer, that of the copolymer with a weight ratio AN/St = 75/25 is 28.0, which is much larger than that of PBMA. In spite of the large differences in solubility parameters, all AN-St copolymers and PS can be toughened by PBMA when the self-compatibilization method is employed (see Tables VIII, IX, and XIV). This indicates that the method of self-compatibilization can be used for a wide range of differences in the solubility parameters of the polymers involved.

CONCLUSION

A novel polymer blend preparation method, self-compatibilization, was developed. In this method, two partially polymerized concentrated emulsions were mixed and subjected to further polymerization, during which homopolymers, copolymers, and network compatibilizers were generated. The networks are formed mostly before an overall conversion of 50 wt %, and their chains are gradually interacting with different linear chains subsequently formed. In this manner the self-compatibilization is achieved. The blends prepared from butyl methacrylate/acrylonitrile-co-styrene and a vinyl-terminated macromonomer via self-compatibilization possess excellent mechanical properties. A significant toughening of acrylonitrile-co-styrene by poly(butyl methacrylate) was observed. The toughness of the

Table XIV Properties of Concentrated Emulsion Blends

AN/St Weight Ratio	Solubilities				Mechanical Properties and (Standard Error)			
	Toluene Removed (Wt %)	THF Removed (Wt %)	DMF Removed (Wt %)	Network Content (Wt %)	Yield Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)	Toughness (MJ/m ³)
0/100	75.4	0	0	24.6	46.8 (1.4)	26 (0.5)	827 (34)	9.7 (0.4)
25/75	19.1	56.6	0	24.3	47.2 (1.2)	30 (1.7)	858 (56)	12.0 (1.1)
50/50	17.8	9.0	43.7	29.4	49.9 (1.9)	61 (4.4)	907 (23)	25.7 (2.4)
75/25	18.9	5.2	49.7	26.2	55.4 (0.6)	22 (0.6)	948 (65)	9.5 (0.2)

Weight ratio of (AN + St)/BMA = 2/1, VTPCL = 5 wt %. Time of partial polymerization of the monomer before the preparation of the concentrated emulsion: 1 h. Time of partial polymerization of concentrated emulsions before mixing: 30 min. Time of polymerization of the mixture of concentrated emulsions: 48 h.

concentrated emulsion blends are five to eight times higher than those of the butyl methacrylate/acrylonitrile/styrene ternary copolymers. Both vinyl-terminated polycaprolactone and vinyl-terminated polybutadiene can be used for the compatibilization. The optimum content of the vinyl-terminated macromonomer in the monomers is about 5 wt %. To obtain good compatibilizing effects, the two concentrated emulsions should be mixed at proper partial monomer conversions (i.e., 10–27 wt % for butyl methacrylate and 7–17 wt % for a mixture of acrylonitrile and styrene). The study of various acrylonitrile/styrene weight ratios showed that the method of self-compatibilization can be used for a wide range of differences in the solubility parameters of the polymers involved.

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