

Halato-Telechelic Polymers. XV. Ionic Cross-Interactions of Immiscible Telechelic Polymers: A Reversible Pathway to Block Copolymer-Type Materials

J. HORRION, R. JÉRÔME, and Ph. TEYSSIE, *Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman B6, 4000 Liège, Belgium*

Synopsis

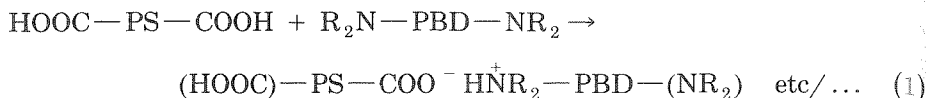
Phase separation of two immiscible polymer blends can be controlled by ionic cross-interactions of the end-groups as promoted by proton transfer from acid end-groups of polymer PA to aliphatic *tert*-amine end-groups of PB. IR spectroscopy supports the occurrence of proton transfer with formation of ammonium carboxylate ion pairs that influences the solution behavior of the blends. Optical microscopy illustrates the opportunity to get finely dispersed blends at a scale of ca. 0.2 μm depending on nature, molecular weight, and functionality of the immiscible polymers and strength of the ion pairs. T_g measurements are in agreement with the general pattern reported for multiphase block polymers, and give consistency to an analogy between finely phase separated blends of acid and *tert*-amine telechelic polymers and related block polymers.

INTRODUCTION

Nowadays much attention is paid to blending commodity and engineering resins as an efficient means for better processability, decrease of cost, and tailoring of properties. Although the interest of homogeneous blends is well-recognized, e.g., Noryl from General Electric Co., multiphase systems have the great advantage to sum up the original properties of each partner and possibly to exhibit some new features in relation to a particular phase morphology. However, the overall physicommechanical behavior of multiphase blends critically depends on their interfacial properties, i.e., a proper interfacial tension allowing a very fine phase dispersion to be reached, and an interphase adhesion strong enough for the established morphology to support applied stresses without disruption. Although block and graft copolymers meet all of these requirements, that is not the case for most immiscible polymer blends. Nevertheless, the lacking proper interphase adhesion of polymer blends can be promoted by the addition of a few percent of a tailored diblock copolymer; the potentialities offered by this emulsification concept have been convincingly illustrated.¹⁻⁴

This very brief discussion stresses that immiscibility of polymers combined with opportunity for local (interphase) interactions is the key point in devising high performance polymer blends. In this regard, the incorporation of specifically interacting groups into the polymers to be blended has been described as a method of increasing miscibility.⁵⁻⁸ Recently, we have reported on the feasibility of "block copolymerizing" immiscible polymers by means of

ionic interactions between different chain ends.⁹ The occurrence of a proton transfer between the two acid end-groups of polystyrene (PS) and the amino group capping both ends of polybutadiene (PBD) has been demonstrated by IR spectroscopy [Eq. (1)]:



The mutual attraction of the resulting carboxylate anions and ammonium cations provides a means of stabilizing the cross-interactions of the immiscible polystyrene and polybutadiene, engaging them in a spatial arrangement (morphology) as block polymers do. The T_g behavior of blends of telechelic polystyrene and polybutadiene terminated with carboxyl and amino groups, respectively, has lent credit to analogy with the related block copolymers. This paper aims at substantiating the formation of ionic linkages between the ends of the immiscible polymers. Four approaches have been considered: (a) solution viscosity, (b) microscopic observations of the phase morphology, (c) T_g behavior in relation to the molecular weight of each prepolymer and the presence of the acid (or amino) groups at both ends of either the styrene or the diene prepolymer, and (d) the main relaxations as observed by thermally stimulated depolarization currents (TSDC).

EXPERIMENTAL

α,ω -Dicarboxylic acid polybutadiene of 4600 molecular weight (MW) was kindly supplied by BF Goodrich (Hycar CTB 2000 \times 156). The carboxylic acid end-groups of Hycar CTB were converted into dimethylamino groups by esterification with *N,N*-dimethylaminoethanol (DMAE), as described elsewhere:⁹ the mean number of amino groups per chain amounted to 1.95. Another polybutadiene sample selectively end-capped by a piperazine group



was estimated from titration of the amino end-groups assuming an ideal functionality of 2. Telechelic polystyrene (PS), poly(α -methylstyrene) (PMS), and polyisoprene (PIP) were prepared by living anionic polymerization in tetrahydrofuran at -78°C . α -Methylstyrene sodium oligomer was used as a difunctional initiator, and *sec*-butyllithium as a monofunctional one. The living polyanions were deactivated by anhydrous carbon dioxide, propanesulfone, and 1-chloro-3-(dimethylamino)propane, respectively, to form the corresponding carboxylic acid, sulfonic acid or *tert*-amino telechelic polymers.¹⁰ Molecular weight was controlled by adjusting the monomer to catalyst molar ratio, and polydispersity did not exceed 1.2. Functionality (f) was determined by potentiometric titration of the acid end-groups with tetramethylammonium hydroxide and of the *tert*-amino end-groups by *p*-toluenesulfonic acid in a 9/1 benzene-methanol mixture; it was better than 1.95 except for disulfonic acid telechelics ($f \sim 1.9$).

Polymer blending and neutralization of amino (or acid) telechelic polymers with a low molecular weight carboxylic acid (or *tert*-amine) were performed by

solvent casting. Each constituent was separately dissolved in toluene (10 wt % for polymer solutions), and a solution was slowly added into the other one under efficient stirring. Two hours later, toluene was allowed for slow evaporation and the final product dried under vacuum at 25°C up to constant weight.

Unless otherwise stated, blend compositions were defined in such a way as the amine to acid molar ratio was 1. IR spectroscopy was performed with a model 197 Perkin-Elmer apparatus. Differential thermal analyses were carried out with a DuPont 990 thermal analyzer from -60°C up to 150°C, at a heating rate of 20°C/min. Each sample was then annealed at 150°C for 15 min before a second run was performed. Molecular weights were determined by size exclusion chromatography in THF at 25°C (Waters 200 apparatus). Samples for electrical measurements were compression molded as 1 mm thick disks at 150°C and then dried *in vacuo* at 110°C for 2 weeks to ensure that the materials were free of residual stress. Apparatus and experimental recipe were described elsewhere.¹¹

RESULTS AND DISCUSSION

Solution Viscosity of Telechelic Polymer Blends

A preliminary study has focused on polybutadiene (PBD) of 4600 MW, selectivity capped at both ends by a carboxylic acid (Hycar from BF Goodrich) and a dimethylamino group, respectively. These two miscible telechelic polymers have been blended within different ratios in order to modify the degree of mutual neutralization of the end-groups. This system is so advantageously free from any thermodynamic repulsion between the polymeric components which might interfere with the effect of ionic cross-interactions of the end-groups. Figure 1 shows that the reduced viscosity of dicarboxylic acid PBD increased as a function of the polymer concentration the more as the percentage of the neutralized acid groups increases. The meaning of the experimental data might be cleared up by plotting the contribution of the intermolecular interactions to the reduced viscosity ($\Delta\eta_{\text{red}}$) versus the degree of neutralization of the acid end-groups. Figure 2 illustrates that dependence at various total polymer concentrations. $\Delta\eta_{\text{red}}$ is the difference between the experimental reduced viscosity of the blend and the theoretical value ($\eta_{\text{red}, m}$) calculated from eq. (2) that relies upon the additivity of the mixed-polymer solution viscosity.¹²

$$\eta_{\text{red}, m} = \frac{C_1}{C_t} \cdot \eta_{\text{red}_1(C_i)} + \frac{C_2}{C_t} \cdot \eta_{\text{red}_2(C_i)} \quad (2)$$

$\eta_{\text{red}_i(C_i)}$ is the reduced viscosity that component i would have in a single polymer solution of concentration $C_t = C_1 + C_2$.

At a constant neutralization degree, $\Delta\eta_{\text{red}}$ increases sharply at increasing polymer concentration. This experimental increase in the solution viscosity can only originate from the cross-interaction of the chain ends and possibly from the electrostatic interaction of the formed ammonium carboxylate ion-pairs. As a result, the apparent chain length of polybutadiene increases together with the opportunity for the chains to overlap each other and to be

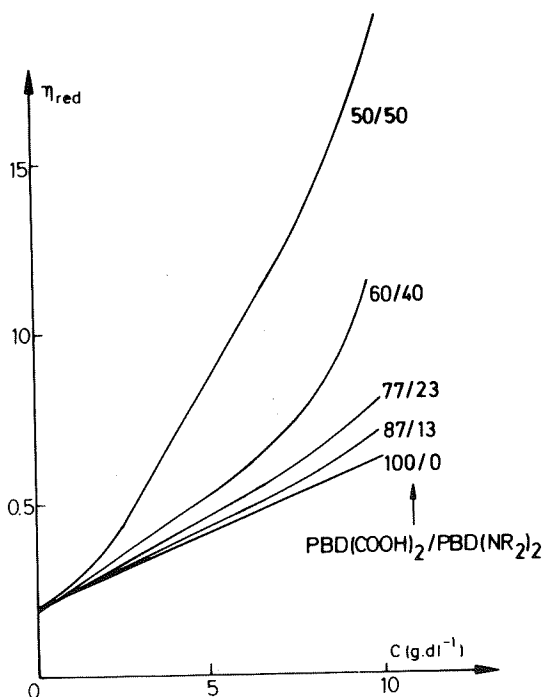
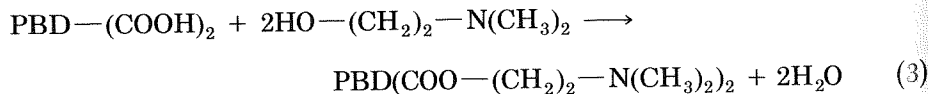


Fig. 1. Reduced viscosity versus polymer concentration plot for α,ω -carboxylic acid polybutadiene blended with various amounts of α,ω -dimethylamino polybutadiene of the same molecular weight (\bar{M}_n : 4600); toluene, 25°C.

ultimately intermingled. This viscosity behavior means that proton transfer is a process restricted to an equilibrium. The ion pair formation is however the more complete as the concentration in acid groups is high and the acid to amine molar ratio close to one. It means that complete neutralization might be reached in the bulk state for a 1/1 acid to amine molar ratio. In the limits of sensitivity of the IR spectroscopy, Figure 3 supports this expectation. The carbonyl stretching band of the initial carboxylic acid groups ($\sim 1710\text{ cm}^{-1}$) has indeed disappeared in the blend in favor of a 1550 cm^{-1} absorption assigned to the carbonyl stretching of carboxylate anion. The absorption observed at 1730 cm^{-1} in the IR spectrum of both the amino telechelic polybutadiene and the final blend has to be attributed to the carbonyl stretching of the ester linkage resulting from the amination of polybutadiene[eq.(3)]:



Although helpful in proving the occurrence of proton transfer from the acid to the amino end-groups, IR spectroscopy is unable to state whether the formed ammonium carboxylate ion pairs can mutually interact or not. In that respect, Figure 4 shows that neutralizing either a carboxylic acid telechelic polymer by

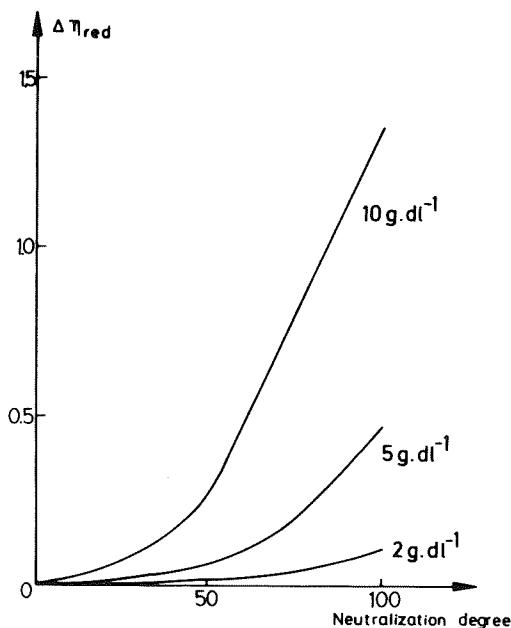


Fig. 2. $\Delta \eta_{red}$ vs. the neutralization degree of α, ω -carboxylic acid polybutadiene (\bar{M}_n : 4600) at various total polymer concentrations. The neutralizing agent is the α, ω -dimethylamino polybutadiene of the same molecular weight. $\Delta \eta_{red}$ is the difference between the experimental value and the reduced viscosity calculated from the additivity of the mixed-polymer solution viscosity [eq. (2)]; toluene, 25°C.

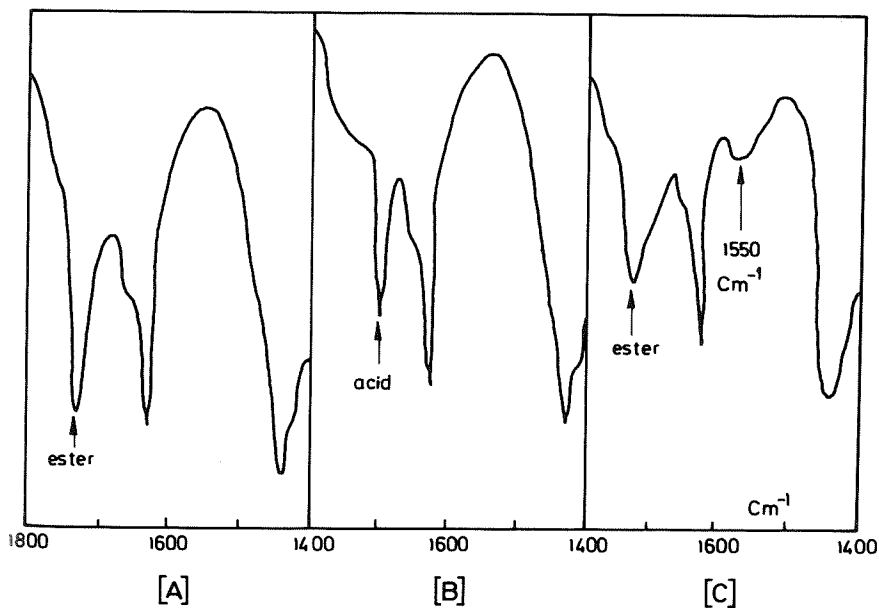


Fig. 3. IR spectra of α, ω -dimethylamino polybutadiene (A) α, ω -carboxylic acid polybutadiene (B), and the related polyblend (C).

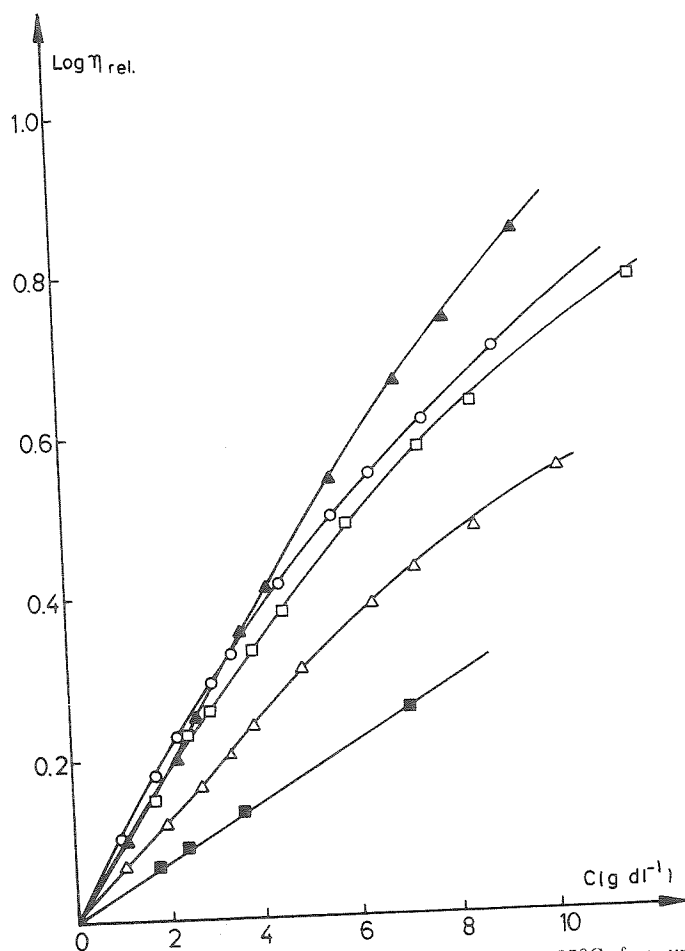


Fig. 4. Relative viscosity-concentration plot in toluene at 25°C for: unfunctionalized polystyrene (1.4×10^4 MW) (■); α,ω -carboxylic acid polystyrene (1.4×10^4 MW) end-neutralized with formic acid (○) and acetic acid (□); α,ω -dimethylamino polystyrene (1.4×10^4 MW) end-neutralized with diisopropylamine (▲) and *N,N*-dimethylbenzylamine (△).

a low MW tertiary amine or a *tert*-amino telechelic polymer by a carboxylic acid also leads to an increase of the solution viscosity. The origin of that effect, which is observed in a nonpolar solvent, has to be found in the dipolar interactions of ammonium carboxylate ion pairs attached at both ends of linear chains. When alkaline or alkaline-earth metal carboxylates are considered, the ion pair interactions are so strong that the solution turns into a gel at polymer concentrations as low as 1–2 wt %.^{10,13} The steric hindrance of the ion pairs might account for the less dramatic change in the solution viscosity that is observed when bulky ammonium carboxylates are concerned. Therefore the solution viscosity of blends of amino and carboxylic acid telechelic polybutadiene should be mainly governed by the ionic cross-interaction of the end-groups and, to a lesser extent, by intermolecular association through the electrostatic interaction of the formed ion pairs.

TABLE I
Molecular and Viscometric Features of Acid and Amino Telechelic Polymers

Polymers	$\bar{M}_n \times 10^{-4}$	$[\eta]^a$ (dL g ⁻¹)	k_H^b
PIP(N(CH ₃) ₂) ₂	1.0	0.115	0.60
PS(COOH) ₂	2.0	0.105	1.50
PS(COOH) ₂	3.0	0.145	1.15
PS(COOH) ₂	4.7	0.265	0.60
PS(COOH) ₂	6.0	0.375	0.56

^aIntrinsic viscosity in toluene at 25°C.

^bHuggins constant.

Extrapolated to blends of immiscible telechelic polystyrene (PS) and polyisoprene (PIP), the previous conclusion means that the ionic cross-interactions of the chain-ends has to associate PS and PIP into species looking like block copolymers. As before, the mean number of chains associated all together should depend on the extent of both the proton transfer between acid *tert*-amino groups and the electrostatic interactions of ammonium carboxylate ion-pairs.

Viscosity of blends of carboxylic acid telechelic PS and dimethylamino telechelic polyisoprene has been measured in toluene at 25°C, the acid to amine molar ratio being systematically one. Nature and molecular weight of the investigated polymers are reported in Table I, together with their viscometric features, i.e., intrinsic viscosity and Huggins constant (k_H).

It is worth recalling that the solution behavior of diblock copolymers has often been described by a model based on the additivity of the intrinsic viscosity of the contributing blocks. Equation (4) has accordingly been proposed by Dondos et al.¹⁴

$$[\eta]_{\text{block}} = ([\eta_1]M_1 + [\eta_2]M_2)/M_{\text{block}} \quad [4]$$

who have reported theoretical intrinsic viscosities very close to the experimental values for poly(styrene-*b*-methylmethacrylate) in a number of solvents. These observations have been supported by Kennedy and Hongu who studied the solution behavior of poly(isobutene-*b*-ethylene glycol) in toluene.¹⁵ Since this model assumes that the unlike blocks do not interact at all, it is known as the "segregated model."

Table II compares the experimental intrinsic viscosity with the value calculated from eq. (4) for blends of α,ω -diamino PIP of 10^4 MW and α,ω -dicarboxylic acid PS of various MW. It can be seen that as the molecular weight of PS increases from 2×10^4 to ca. 5×10^4 , the solution behavior of the blend comes in a closer agreement with the model of a segregated diblock copolymer. When the 6×10^4 MW PS is combined with the 10^4 MW PIP the proton transfer between the end-groups is no longer important enough to promote the apparent formation of diblock species. The decreasing association of PS and PIP when molecular weight of PS increases, i.e., when the acid content of PS decreases, is in a qualitative agreement with a shift of the

TABLE II
 Intrinsic Viscosity and Huggins constant (k_H) of Blends of PIP(NR₂)₂ ($\bar{M}_n: 10^4$)
 and PS(COOH)₂ in Toluene at 25°C

PS(COOH) ₂ $\bar{M}_n \times 10^{-4}$	$[\eta]_{\text{exp}}$ (dL gr ⁻¹)	$[\eta]_{\text{theor}}$ diblock	$\Delta[\eta]^a$ (%)	k_H
2.0	0.170	0.108	+60	1.43
3.0	0.195	0.137	+41	1.22
4.7	0.255	0.237	+7	1.77
6.0	0.315	0.337	-6	0.61

^a $\Delta[\eta]$: Intrinsic viscosity change compared to the theoretical value as calculated for a diblock copolymer.

equilibrium of the proton transfer process at the expense of the ammonium carboxylate ion-pairs.

Finally, it should be noted that, except for the 6×10^4 MW PS containing blend, the Huggins constant (k_H) is much greater than the values generally reported (0.3–0.5) for a random coil in a good solvent.¹⁶ Abnormally high values of k_H are usually attributed to aggregation phenomena and could therefore agree with the partial association of the blended polymers. In this regard, two observations reported by H. Morawetz deserve interest. The author has investigated the solution viscosity of mixtures of two different acidic and basic copolymer pairs. PS containing 5.8% of vinylpyridine units and polymethylmethacrylate (PMMA) containing 8.5% of methacrylic acid form the first pair,¹⁷ whereas the second one is constituted with PMMA containing 4.9% of acid units and 5.8% of dimethylamino ethyl groups, respectively.¹⁸ The slope of a reduced viscosity plot for the first mixture was found to be intermediate between the slope of similar plots of either component of the mixture. This observation was in sharp contrast to the steep slope of the reduced viscosity plot of the second mixture. This apparent contradiction can be actually rationalized by the difference in basicity of aromatic and aliphatic tertiary amines. As experimentally observed by Rees, aromatic amines are too weak to react with carboxylic acid-containing polyethylene, whereas the acid pendant groups are neutralized with aliphatic amines.¹⁹ It means that no proton transfer occurs from the carboxylic acid to the pyridine unit of the first pair investigated by Morawetz, and no anomaly arises from the slope of the reduced viscosity plot of the blend, i.e., from the Huggins constant. Ammonium carboxylates are easily formed in the second mixture and the mutual interaction of the two copolymers accounts for a substantially higher value of k_H .

Phase Morphology of Telechelic Polymer Blends

The major difference between immiscible polymer blends and the related block copolymers has to be found in the fineness of the phase dispersion. The gross phase separation that occurs usually in immiscible polymer blends is prevented in block copolymers by the chemical bonding of the polymeric constituents. Therefore the phase morphology of immiscible acid and amino

telechelic polymers could provide a support to the suggested analogy with block copolymers.

A mixture of a commercial amino-telechelic PBD [$\text{PBD}(-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NH}_2)_2$; 4000 MW] and an unfunctionalized PS (3×10^4 MW) has been selected as a reference of immiscible polymers free from any specific cross-interactions of the end-groups. Expectedly, very coarse separated phases are observed by phase contrast optical microscopy (Fig. 5). The PS constituent of the reference blend has then been modified by capping the two extremities by a carboxylic acid and a sulfonic acid, respectively. The expected proton transfer from the carboxylic acid to the amine is responsible for a substantial decrease of the phase dimensions that are now close to a few microns. A more dramatic change occurs when sulfonic acid groups are involved, since no phase separa-

: 10^4)

k_H

1.48
1.22
1.77
0.61

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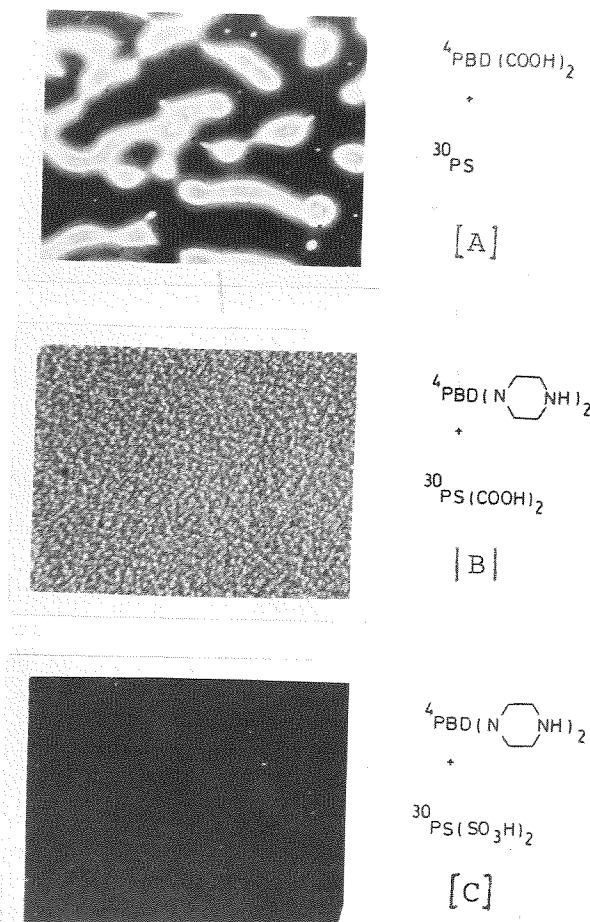


Fig. 5. Optical microscopy of polybutadiene (PBD) and polystyrene (PS) blends. Molar ratio of the end-groups = 1. (A) $\text{PBD}(\text{COOH})_2$ (\bar{M}_n : 4600) and PS (\bar{M}_n : 30,000); (B) $\text{PBD}(-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NH}_2)_2$ (\bar{M}_n : 4000) and $\text{PS}(\text{COOH})_2$ (\bar{M}_n : 30,000); (c) $\text{PBD}(-\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NH}_2)_2$ (\bar{M}_n : 4000) and $\text{PS}(\text{SO}_3\text{H})_2$ (\bar{M}_n : 30,000).

tion can be detected anymore by optical microscopy, i.e., phases have an average size smaller than 0.2μ . It is thus obvious that the deleterious effects that the immiscibility has on the phase morphology of polymer blends can be largely overcome by promoting ionic cross-interactions between the chain-ends of the partners. The strength of these interactions is a key point in restricting the phase separation and quite expectedly ammonium sulfonates are much stronger and thus more efficient than ammonium carboxylates.

Actually, the state of mixing results from a balance between two opposite tendencies: the thermodynamic immiscibility that increases with chain length and the effect of the ionic intermolecular interactions that decreases at increasing molecular weight.

As a result, the higher the molecular weight of the blended polymers, and the less efficient the ionic interactions of the chain ends in preventing an extensive phase separation. This expectation is supported by the three micro-

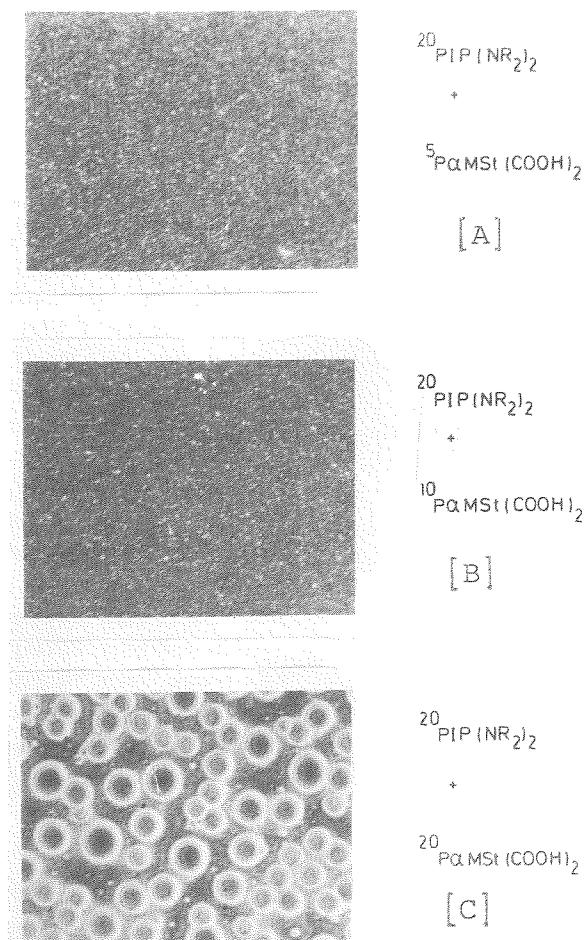
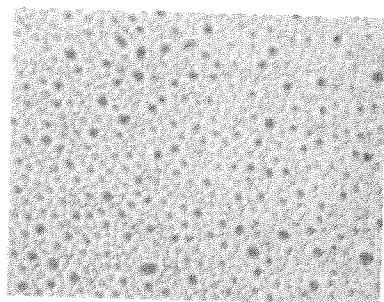


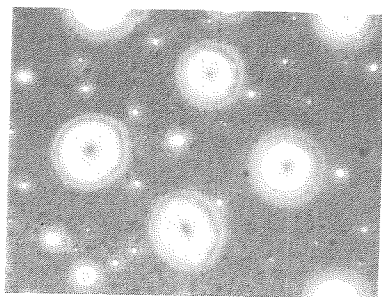
Fig. 6. Optical microscopy of α,ω -dimethylamino polyisoprene ($\bar{M}_n: 2 \times 10^4$) blended with α,ω -carboxylic acid poly α -methylstyrene of 5×10^3 MW (A), 10^4 MW (B), and 2×10^4 MW (C): $[\text{NR}_2]/[\text{COOH}] = 1$.


 20
 $\text{PIP}(\text{NR}_2)_2$

+

 30
 $\text{PS}(\text{COOH})_2$

[A]


 20
 $\text{PIP}(\text{NR}_2)_2$

+

 25
 $\text{PS}(\text{COOH})_1$

[B]

Fig. 7. Optical microscopy of α,ω -dimethylamino polyisoprene ($\bar{M}_n: 2 \times 10^4$) blended with α,ω -carboxylic acid polystyrene ($\bar{M}_n: 3 \times 10^4$) (A), and ω -carboxylic acid polystyrene ($\bar{M}_n: 2.5 \times 10^4$) (B). $|\text{NR}_2|/|\text{COOH}| = 1$.

graphs of Figure 6, where dimethylamino telechelic PIP of 2×10^4 MW has been blended with carboxylic telechelic poly α -methylstyrene (PMS) of various molecular weights, while keeping as 1 the acid to amine molar ratio.

As long as the PMS molecular weight does not exceed 10^4 , the formation of ammonium carboxylate ion pairs is the more thermodynamically favored process and PIP and PMS are intimately mixed at the micron scale. When the molecular weight of PMS is 2×10^4 , the ionic cross-interactions of the chain ends are no longer able to counterbalance the polymer demixing which contributes now favorably to the free energy of the blend. As a last piece of information, Figure 7 shows that the functionality of the blended polymers is of great importance. Although mixing α,ω -dicarboxylic acid PS of 3×10^4 MW with the diamino PIP used in the previous series does not lead to a gross phase separation, using ω -carboxylic acid PS of a similar molecular weight (25,000) is responsible for a dramatic phase separation. This result is not amazing, since the monofunctional PS of 25,000 MW is formally equivalent to a difunctional PS having as twice as high a molecular weight (5×10^4). From the comparison of Figures 6 and 7, it can be concluded that PIP/PMS pair is less miscible than the PIP/PS.

TABLE III
Molecular Features and Glass Transition Temperature (T_g) of Acid and *tert*-Amine
Telechelic Polystyrene and Polyisoprene

Polymer	$\bar{M}_n \times 10^{-4}$	Functional groups		T_g (°C)
		Nature	mol %	
Polystyrene (PS)	2.0	COOH	1.05	92
	3.0	COOH	0.70	100
	4.7	COOH	0.45	100
	6.0	COOH	0.35	100
	3.0	SO ₃ H	0.70	100
	6.0	SO ₃ H	0.35	100
	1.3	N(CH ₃) ₂	1.60	96
	Polyisoprene (PIP)	0.65	COOH	2.10
1.5		COOH	0.90	-5
2.0		COOH	0.70	-5
3.0		COOH	0.45	-5
3.7		COOH	0.37	-5
4.5		COOH	0.30	-5
1.0		N(CH ₃) ₂	1.35	-2
2.0		N(CH ₃) ₂	0.70	-2

Glass Transition Temperature of Telechelic Polymer Blends

Glass transitions of blends of carboxylic acid telechelic PS (ca. 5×10^3 MW) and amino telechelic PIP (ca. 4000 MW) have been reported in a preliminary study.⁹ Two T_g 's were systematically observed: the first one was very close to T_g of PBD and the second one was ca. 30°C below the usual one of PS. A similar situation can be found in block copolymers²⁰⁻²⁸ and the decrease in T_g of the rigid phase is generally accounted for either by some phase mixing at the border of the microdomains or by induction of premature motions in the rigid phase by the highly mobile associated blocks.^{21,26}

In some blends, an intermediate T_g was observed which disappeared however after an appropriate thermal treatment.^{28,29} This behavior provides a further similarity with multiphase block copolymers which can exhibit a third T_g intermediate to those of each constitutive block depending on solvent and thermal treatment, thus revealing some nonequilibrium state of mixing.

In order to support these very preliminary results, two series of blends of dimethylamino telechelic PIP and acid telechelic PS of different molecular weights have been characterized, where molecular weight of PIP is 10^4 and 2×10^4 in the first and the second series of blends, respectively. PS is selectively end-capped by a carboxylic acid group and in some instances, by a sulfonic acid group. T_g , molecular weight, nature and mole percentage of the end-groups of the available telechelic polymers are summarized in Table III.

TABLE IV
Experimental and Theoretical Glass Transition Temperatures of Blends of Dimethylamino
Telechelic Polyisoprene ($\bar{M}_n: 10^4$) and Acid Telechelic Polystyrene of Various \bar{M}_n

T_g (°C)	Telechelic polystyrene			Glass transition temperature (°C)				
	$\bar{M}_n \times 10^{-4}$	End-groups	Wt %	Experimental		Theoretical		
				a	b	c	d	e
92								
100								
100	2.0	COOH	66	44	48	58	45	57
100	3.0	COOH	75	49	67	68	60	71
100	4.7	COOH	82	51	69	77	69	79
100	6.0	COOH	86	50	71	81	75	84
100								
	3.0	SO ₃ H	75	55	55	68	60	71
96	6.0	SO ₃ H	86	60	59	81	75	84

^a Blends as prepared by solvent casting and drying at 25°C.

^b Blends annealed at 150°C for 15 min.

^c According to Fox.³⁰

^d According to Di Marzio and Gibbs.³¹

^e According to Pochan et al.³²

Blends of Amino Telechelic PIP of 10^4 MW and Acid Telechelic PS of Various MWs

Table IV reports T_g 's of films prepared by toluene casting and drying *in vacuo* (25°C) together with T_g 's of blends annealed at 150°C for 15 min. Only one T_g is detected in sharp contrast to the previously investigated blends of short length PS and PBD.⁹ Thus the PS/PIP pair should be less immiscible than the PS/PBD pair as it might be anticipated from the phase morphology illustrated in Figures 5 and 7. This could be due to the completely different microstructure of the polydiene chains used in the two studies. PBD is indeed constituted with 85% of 1,4-units whereas PIP contains only 3.4 (65%) and 1.2 (35%) units. It means that the contour chain length of PBD should be nearly twofold greater than that of PIP of the same molecular weight. As a rule, T_g increases upon annealing at 150°C, except for blends containing sulfonic acid telechelic PS that are insensitive to the thermal treatment. After solvent casting, blends of carboxylic acid telechelic PS exhibit a glass transition lower than T_g of blends of the sulfonic counterpart, whereas the inverse situation is reported after annealing at 150°C.

Finally, T_g of the annealed blends does not correspond to values calculated for homogeneous blends from theoretical relationships proposed by Fox,³⁰ Gibbs-Di Marzio,³¹ and Pochan,³² respectively.

All in all, these experimental observations mean that some degree of chain intermixing is promoted by ionic cross-interactions of PS and PIP, but the possible electrostatic association of the ammonium carboxylate or sulfonate ion-pairs is able to freeze-in nonequilibrium situations in the solvent-cast blends. Mutual interactions of ammonium carboxylate ion pairs are however weak enough to allow the system to rearrange at 150°C and to exhibit T_g 's

closer to the theoretical values. Similarly, the comparatively small change in T_g exhibited by the shortest PS chains containing blend is consistent with a much more difficult rearrangement when the ion pair content is sufficiently high. Furthermore, since the sulfonate-type ion pairs are known to interact more strongly than the carboxylate ones, it is not surprising that the situation frozen-in during casting is stable against annealing at 150°C.

In conclusion, T_g 's of the annealed blends as reported in Table IV are most likely not characteristic of systems in their thermodynamic equilibrium state. It should also be stressed that it is not clear at all whether the previously mentioned relationships should predict T_g correctly due to the possible disturbing effect of the ion-pairs on free volume. It is of interest to compare results of Table IV with those reported by Eisenberg et al. for the same pair of PS and PIP chains modified by randomly attached sulfonic acid and aromatic amine (pyridine), respectively.^{6,8} These authors mention that the polymer miscibility is observed by differential calorimetry (DSC) when the functional groups are present at a level of ca. 5 mol %, i.e., approximately 5–10-fold higher than in the telechelic polymer blends. This apparent discrepancy can be mainly rationalized by the higher molecular weight of the copolymers used by Eisenberg et al. Obviously, the higher the chain length of the blended polymers, and the greater the intrinsic immiscibility that has to be counterbalanced by favorable intermolecular interactions.

The expectedly higher mobility of the functional groups when selectively attached at both ends of linear chains rather than randomly to long polymeric backbones might also contribute to the apparent disagreement between the two studies.

Blends of Amino Telechelic PIP of 2×10^4 MW and Acid Telechelic PS of Various MWs

A twofold increase of the PIP molecular weight has a very significant effect on the T_g behavior. Two T_g 's are indeed detected, which means that a phase separation is extended enough to allow two types of phases to be identified by DSC. A first T_g is observed in the same temperature range as T_g of the initial PIP; nevertheless, this T_g is not sharp enough to be measured accurately and discussed in a reliable way. The second T_g behaves quite similarly to the unique T_g of the previous series of blends upon the effect of the thermal treatment, PS molecular weight and nature of the acid end-groups (Table V). Despite a pronounced phase separation, T_g of the rigid phase is still much smaller than T_g of the initial PS.

Blends of Amino Telechelic PS of 13,000 MW and Acid Telechelic PIP of Various MWs

A third series of blends has been investigated wherein the amino groups are now attached to PS and the acid groups to PIP (Table VI). Although the molecular weight of the polymers associated in the first and the third series of blends is similar, these systems have to be distinguished not only by the inversion of the functional groups attached at both ends of PS and PIP, but also by the weight composition that ranges from 66 to 86% PS in Table IV and from 22 to 67% PS in Table VI.

TABLE V
Glass Transition Temperatures of Blends of Dimethylamino Telechelic Polyisoprene ($\bar{M}_n: 2 \times 10^4$) and Acid Telechelic Polystyrene of Various \bar{M}_n s

$\bar{M}_n \times 10^{-4}$	Telechelic polystyrene		T_g^a (°C)	
	End-groups	Wt %	^b	^c
2.0	COOH	50	60	62
3.0	COOH	60	50	80
4.7	COOH	70	52	^d
6.0	COOH	75	54	82
3.0	SO ₃ H	60	55	55
6.0	SO ₃ H	75	(d)	65

^a T_g reported on the high temperature side of thermograms.

^bBlends as prepared by solvent casting and drying at 25°C.

^cBlends annealed at 150°C for 15 min.

^dUndetermined.

These modifications are clearly responsible for a substantial difference in T_g behavior. In contrast to the first series, blends of the third one are immiscible as evidenced by at least two clear-cut T_g 's. After solvent casting and drying, blends containing low molecular weight PIP (2×10^4 and 1.5×10^4) exhibit however an intermediate T_g which disappears after annealing at 150°C and is indicative of an incompletely developed phase separation. This observation supports a similar effect reported in the previous study dealing with the PBD/PS pair.⁹

When the PIP component is still shorter (6500 MW), the partial mixing of PS and PIP increases since the intermediate T_g is no longer observed on behalf of a unique low temperature T_g that appears at an abnormally high temperature, compared to the other blends. This situation of uncomplete

TABLE VI
Glass Transition Temperatures of Blends of Dimethylamino Telechelic Polystyrene ($\bar{M}_n: 2 \times 10^4$) and Carboxylic Acid Telechelic Polyisoprene of Various \bar{M}_n s

Telechelic polyisoprene		Glass transition temperature (°C)				
$\bar{M}_n \times 10^{-4}$	Wt %	First DSC run ^a			Second DSC run ^b	
		T_{g1}	T_{g2}	T_{g3}	T_{g1}	T_{g2}
4.5	78	- 5		26	- 10	70
3.7	74	- 2			- 9	66
3.0	70	- 10		66	- 11	58
2.0	60	- 16	19	52	- 20	52
1.5	54	- 20	12	48	- 23	52
0.65	33		9	65	- 10	64

^aBlends as prepared by solvent casting and drying at 25°C.

^bAfter annealing at 150°C for 15 min.

phase separation is again unstable against further annealing. Thermal treatment dramatically improves the sharpness of the PS and PIP phase separation, but not to an extent providing T_{g1} with the same value as the two other next blends (PIP of 1.5×10^4 and 2×10^4 MW). This general behavior is in qualitative agreement with that of diblock and multiblock poly(styrene-*b*-isoprene) in which the molecular weight of PS is kept constant and that one of PIP varies. Block copolymers with high isoprene content form two phases, whereas, at the other extreme, a single glass transition is observed.²² Another analogy with block copolymers can be found in T_g of the soft phase (T_{g1}) which, after annealing, is systematically smaller than that of the initial PIP. The same observation has been reported for polydiene containing block copolymers, such as poly(styrene-*b*-butadiene),³³ multiblock poly(aramid-*b*-butadiene),³⁴ and high impact polystyrene.^{35,36}

In order to account for that effect, it has been argued that the two main phases do not contract in the same way when the multiphase copolymer is cooled from the melt down to T_g of the rubbery component. Indeed below T_g of the rigid phase, the soft phase goes on contracting and accordingly favors the formation of voids which increases the free volume of the rubber and decreases its T_g .³³ A last important point to be stressed is the constancy of T_g of the rigid phase upon annealing. It should mean that changing the way in attaching the ion pair to the constitutive polymers has a deep effect on the ability of these dipoles to freeze nonequilibrium situations during solvent evaporation. Although tentative, this explanation finds an experimental support in independent observations. When a carboxylic acid telechelic PS is neutralized by a metal cation or an amine, a decrease of T_g is usually reported when the polymer is characterized after recovering from solvent and drying below T_g .³⁷ Annealing at temperatures above T_g is required to observe a T_g close to and possibly higher than T_g of the unneutralized material.³⁸ In contrast, neutralizing by a carboxylic acid the *tert*-amino telechelic PS of the same molecular weight as before does not allow a T_g depression to be observed for samples only dried below T_g .³⁹ Whatever the origin of that unexpected effect, it is worth noting that T_g of the rigid phase is again much smaller than the theoretical value (96°C), and this is of course in agreement with the usual behavior of block copolymers.

In conclusion, the investigation of the T_g behavior completely supports the previously suggested analogy between blends of immiscible amino and acid telechelic polymers and the related block copolymers, i.e., systems in which the ends of the chemically different chains are covalently bonded to each other. In the blends under investigation, no permanent linking between the chain-ends is promoted but rather thermoreversible and dynamic ionic cross-interactions. This type of bonding might have a retarding effect on the phase separation process.

The possible electrostatic interaction of the ion pairs can indeed favor intermolecular associations which should decrease the chain mobility and retard the attainment of the equilibrium state. Since the behavior is mainly temperature-dependent, it should be of interest to follow, i.e., by small angle x-ray scattering, the change in the phase morphology promoted by an appropriate thermal treatment.

Glass Transition as Observed by Thermally Stimulated Depolarization Currents

It is worth stressing that the previous discussion mainly relies upon criteria based on glass transition. A binary blend is declared immiscible when the usual T_g of each component is observed, whereas the observation of only one intermediate T_g is accepted as an indication for miscibility. It is well-known that the ability of different experimental techniques in detecting T_g differs from one to another. In this respect, differential scanning calorimetry is likely one of the least sensitive techniques. It is the reason why some representative blends have been further characterized by a higher resolution technique: measurement of the thermally stimulated depolarization currents (TSDC). The principle and performances of this technique have been described elsewhere.^{40, 41}

Figure 8 shows how the intensity of TSDC depends on temperature for three particular blends. According to DSC, blends of amino telechelic PIP of 2×10^4 MW (Table V) exhibit two T_g s, although the low T_g is not sharp enough to be determined accurately. The TSDC plot concludes unambiguously to the existence of 2 T_g s, for instance at -23 and 88°C when PS of 6×10^4 MW is considered. It must be recalled that T_g as determined by two different techniques must always be compared cautiously. The experimental values may be different as a consequence of the time-dependent property of glass transition.

Furthermore, an ionic migration generally superimposes to any other relaxation process occurring at high temperature when TSDC are recorded: the

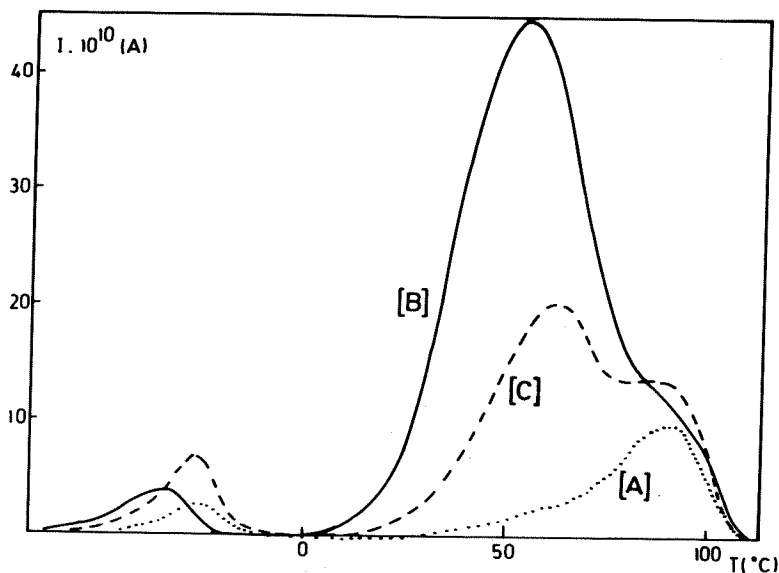


Fig. 8. TSDC curves of α, ω -dimethylamino polyisoprene (PIP) and α, ω -carboxylic acid polystyrene (PS) blends. $[\text{NR}_2]/[\text{COOH}] = 1$. Polarization at 150°C , under a 100 kV/cm dc electrical field, for 10 min. Curves recorded at a 6°C min. rate: (A) PIP (2×10^4 MW)/PS (6×10^4 MW) (....); (B) PIP (10^4 MW)/PS (4.7×10^4 MW) —; (C) PIP (10^4 MW)/PS (6×10^4 MW) (---).

position of the peak attributed to the α -relaxation of PS might thus be shifted towards higher temperatures by several degrees. DSC measurements have also shown that reducing the PIP molecular weight from 2×10^4 to 10^4 promoted the polymer miscibility (Tables IV and V). TSDC plots disagree with that conclusion since, besides the α -relaxation of PIP, a two-component relaxation is observed on the higher temperature side of the curves (Fig. 8). The shoulder to the main peak might be assigned to well phase separated PS. The main peak, the relative importance of which increases as the PS molecular weight decreases, might be a clear evidence for a partial mixing of PIP and PS. As a rule, TSDC results are not contrasted with DSC conclusions, but, as illustrated by Figure 8, the TSDC technique gives a more detailed insight on the phase morphology of the polyblends.

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Erratum

Halato-Telechelic Polymers. XV. Ionic Cross-Interactions of Immiscible Telechelic Polymers: A Reversible Pathway to Block Copolymer-Type Materials

J. HORRION, R. JÉRÔME and PH. TEYSSIE, *Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman B6, 4000 Liège, Belgium*

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The following corrections are to be noted:

p. 158 Fig. 4 Caption: (■); α,ω -dimethylamino polystyrene (instead of α,ω -carboxylic acid polystyrene)

(□); α,ω -carboxylic acid polystyrene (instead of α,ω -dimethylamino polystyrene)

p. 159 Paragraph 1, line 5 should read "... the proton transfer from acid to *tert*-amino groups ..."

p. 164 Paragraph 1, line 2 should read "... amino telechelic PBD (instead of PIP)

p. 167 Table VI Caption: (\bar{M}_n : 1.3×10^4) instead of (\bar{M}_n : 2×10^4)