

# Miscibility Behavior and Coil Overlap in Ionic Blends of Phenylated Polytriphenylene Oxide and Poly(Methyl Methacrylate)

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**ABSTRACT:** Blends of sulfonated phenylated polytriphenylene oxide and poly(methyl methacrylate-co-4-vinyl pyridine) were examined by dynamic mechanical, Fourier transform infrared, and NMR techniques. A high degree of miscibility was evident from a single drop in a plot of the storage modulus versus the temperature. The presence of ionic moieties due to proton transfer from sulfonic acid to 4-vinyl pyridine was confirmed by both NMR and IR spectroscopy studies. The coils were found to be close to one another in dimethyl sulfoxide-*d*<sub>6</sub> because the aromatic shielding effect of the phenyl rings of the pheny-

lated polytriphenylene oxide units was observed from the upfield shift of most of the protons of poly(methyl methacrylate) in the NMR spectrum. However, the absence of cross peaks in the nuclear Overhauser and exchange spectroscopy experiments suggested that the intermolecular distance between the chains had to be larger than 4 Å. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 728–733, 2003

**Key words:** infrared spectroscopy; ionomers; miscibility; compatibilization

## INTRODUCTION

Miscibility enhancement in polymers has been an active field of research in the past 2 decades, and many enhancement techniques have been used.<sup>1–15</sup> Ionic interactions have received special attention as a particularly efficient method of miscibility enhancement in several highly dissimilar systems.<sup>16–20</sup> In some cases, miscibility has been due to a proton transfer from an acidic site on one polymer to a basic site on another, leading to ion–ion interactions.<sup>16–19</sup> In others, the transfer of a metal cation from an ionomer to a polar polymer as a result of ion–dipole interactions has been involved.<sup>20,21</sup>

Many techniques are available for investigating miscibility in polymer blends.<sup>22</sup> For example, light scattering can be used to probe dimensions of the order of the wavelength of light (ca. 1000–10,000 Å), dynamic mechanical studies of the glass transition are sensitive to dimensions of about 100 Å, and fluorescence techniques and electron microscopy methods are useful at still smaller dimensions. More recently, NMR spectroscopy has been used in ionic blends, and it offers information about distances as small as a few angstroms.<sup>23</sup>

Studies that have focused on the formation of ionomer blends from highly dissimilar materials, such as fluorocarbons and hydrocarbons<sup>24</sup> or aromatics and aliphatics of widely differing glass transitions,<sup>19</sup> have shown that in the absence of ionic interactions, these materials are immiscible.

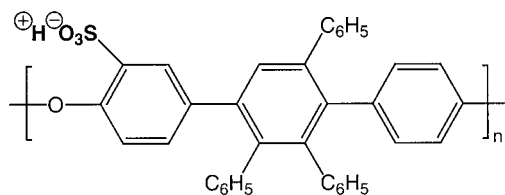
This study is an extension of a previous work on blends containing phenylated polytriphenylene oxide (ØPTØO) and poly(ethyl acrylate) (PEA) polymers of widely differing glass transitions. In that system, ØPTØO and PEA homopolymers were modified by the introduction of carefully chosen ionic groups, that is, sulfonic acid on ØPTØO and 4-vinyl pyridine (4VP) on PEA, as shown:

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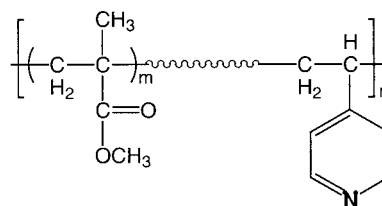
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**HSO<sub>3</sub>-Phenylated  
Poly(triphenylene oxide)**



**Poly(methyl  
methacrylate-co-4-VP)**

Miscibility enhancement was achieved by proton transfer from sulfonic acid on ØPTØO to 4VP on PEA. This was clearly evident from the dynamic mechanical properties in which a single but broad descent in the storage modulus ( $G'$ ) curve was seen for blends of functionalized polymers with an equivalent weight (EW) of 600 or less. However, very little information regarding the specific molecular nature of the interaction is available on this system. The fundamental issues regarding these systems consist, specifically, of whether the aromatic chains are in close proximity to the acrylate chains and how rapidly the coils interpenetrate in solution. In principle, NMR is capable of answering these questions because the protons give resonance peaks at different positions depending on whether or not they are in the vicinity of the aromatic groups.<sup>23</sup> It is more convenient to look at the aromatic shielding effect on methoxy protons than that on  $-\text{CH}_2-$  protons, and so in this study, we look at the molecular-level miscibility enhancement process with poly(methyl methacrylate) (PMMA) instead of PEA. The methoxy protons show a larger shielding effect than the ethoxy protons in the acrylic group; therefore, for our NMR investigation, there is a considerable advantage in using the ØPTØO/PMMA system instead of the ØPTØO/PEA system, which was used in mechanical property studies.

The coil overlap process was studied in some detail for a sulfonated polystyrene/poly(methyl methacrylate-co-4-vinyl pyridine) (PMMA-4VP) blend system in a dimethyl sulfoxide (DMSO) solution by NMR.<sup>23</sup> In that study, it was found that proton transfer from the sulfonic acid group to the 4VP ring was a rapid process, but the alignment of the polymer chains due to coulombic forces was a slow one. The existence of considerable coil overlap was seen from the upfield shifting of most of the protons on the methyl methacrylate repeat units caused by the aromatic shielding effect of the phenyl rings of the styrene units. This process reached a steady-state value only after approximately 2 h for a sample containing about 10 mol % of interacting groups. That study showed that mixing, even in solution, was slow, and it suggested that the mixing conditions were perhaps even more impor-

tant in ionomer blends than in other systems. Therefore, because the methoxy and  $\alpha$ -methyl protons of PMMA are also expected to be sensitive to the presence of aromatic rings in ØPTØO, it should be possible to study the coil overlap process in this system. This has, indeed, been accomplished.

For the sake of completeness, the miscibility behavior is also evaluated from dynamic mechanical measurements with a torsion pendulum, as previously done.<sup>19</sup> Finally, the presence of ionic moieties resulting from the proton-transfer mechanism and a semi-quantitative evaluation of the extent of this process are studied by IR spectroscopy.<sup>25</sup>

## EXPERIMENTAL

### Materials

A methyl methacrylate copolymer containing 11 mol % 4VP (EW = 910) was synthesized, in connection with other projects,<sup>23,26</sup> by free-radical copolymerization. Benzoyl peroxide was employed as an initiator in the reaction. A complete description of the synthesis and properties of the copolymer has been given elsewhere.<sup>26</sup> All samples were dried at 60°C to a constant weight under vacuum before dissolution and mixing.

ØPTØO was sulfonated, also in connection with other projects,<sup>19,27</sup> with a slightly modified version of the procedure of Makowski et al.<sup>28</sup> The polymer properties before sulfonation were as follows: number-average molecular weight =  $1.4 \times 10^3$  g/mol, polydispersity index = 3.4, and intrinsic viscosity = 0.8 dL/g. The details of the sulfonation and some properties of the resulting materials have been given elsewhere.<sup>27</sup> In this work, sulfonated phenylated polytriphenylene oxide (SØPTØO-Acid), with an EW of 1080, was used for blending with a methyl methacrylate copolymer containing 11 mol % 4VP (PMMA-4VP; EW = 910).

### Blending

For the dynamic mechanical study, SØPTØO-Acid and PMMA-4VP were dissolved together in DMSO

(1% w/v) at 90°C with a stirred autoclave and mixed for 3 h. The mixture (54.3/45.7 w/w) contained stoichiometric amounts of sulfonic acid and 4VP groups. The sample was recovered by the evaporation of the solvent at progressively higher temperatures (from room temperature to 80°C). The material was then dried initially at 80°C for 1 week and later at 120°C for 2 weeks under vacuum before being molded.

### Instrumental methods of analysis

#### Dynamic mechanical studies

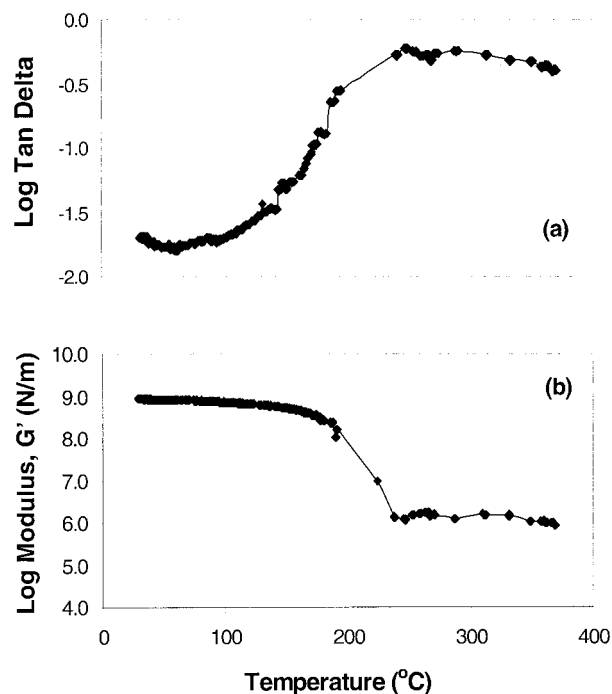
The sample for the dynamic studies was prepared by compression molding at 220°C with a maximum pressure of 45 MPa for 15 min. The molded sample was then stored under vacuum at 120°C for 1 week before the dynamic mechanical measurements. The dynamic mechanical studies were performed with a homemade computerized torsion pendulum in the temperature range of 25–400°C at frequencies varying from 4 to 0.1 Hz. A heating rate of about 1°C/min was employed during the experiment.

#### IR spectroscopy studies

IR spectroscopy studies were carried out on a Nicolet model 7000 Fourier transform infrared (FTIR) spectrophotometer (Madison, WI). The samples were prepared by the dissolution of a polymer mixture containing stoichiometric amounts of interacting acidic and basic groups in DMSO (1% w/v) at room temperature. A small portion of the mixture was then cast directly onto a NaCl window that was subsequently dried in a vacuum oven at 80°C for 1 week before use. The number of scans per spectrum was 128, and the number of data points per scan was 16,384, corresponding to a resolution of 1 cm<sup>-1</sup>. The semiquantitative analysis was based on the ratio of the intensities of the acrylate groups in PMMA and the 4VP groups in modified PMMA before the interaction with the sulfonated polymer. Therefore, the acrylate group in the PMMA acted as an internal standard.

#### NMR studies

NMR spectra were taken on a Varian XL-300 spectrometer (Palo Alto, CA) at 90°C for samples of sulfonic acid phenylated polytriphenylene oxide (PT-O-Acid), PMMA-4VP, and a blend of the two in DMSO. The blend composition was calculated to correspond to an equimolar ratio of sulfonic acid groups and pyridine rings. The polymers were weighed in an NMR tube, the solvent (100% deuterated DMSO) was added to achieve a total concentration of about 2 wt %, and the sample was immediately placed in the NMR probe at 90°C. Spectra were taken after 1 and 2 h.



**Figure 1** Variation of (a)  $\tan \delta$  and (b)  $G'$  with temperature for a stoichiometric blend of SØPTØO-Acid and PMMA-4VP (54.3/45.7 w/w).

## RESULTS AND DISCUSSION

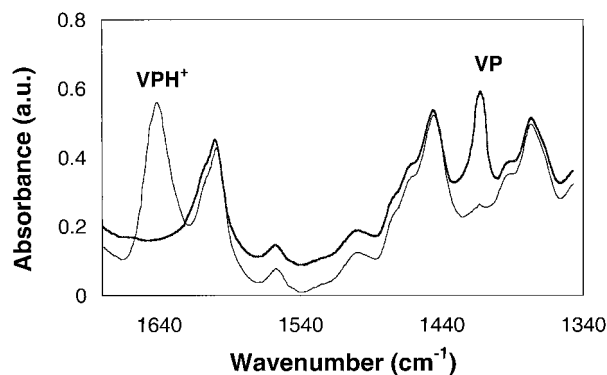
### Dynamic mechanical results in the transition region

The glass-transition values of unblended PMMA-4VP and SØPTØO-Acid were found to be 127<sup>26</sup> and 331°C,<sup>27</sup> respectively, by differential scanning calorimetry (DSC).

The variation of  $G'$  and the loss tangent ( $\tan \delta$ ) with the temperature for a stoichiometric blend of SØPTØO-Acid and PMMA-4VP (54.3/45.7 w/w) is shown in Figure 1. The absence of a two-step descent in the  $G'$  curve, as well as the absence of two  $\tan \delta$  peaks corresponding to the glass-transition temperatures of the individual components (indicated by arrows on the temperature axis), suggests strong miscibility. A single drop in the  $G'$  curve in the region of the glass transition of the blend should be noted. This suggests a considerable level of miscibility. However, the shape of the  $\tan \delta$  curve above the glass transition suggests that some heterogeneity may be present. It is interesting to note that the level of miscibility seen here at 11 mol % 4VP was achieved in the ØPTØO/PEA system at a concentration of 16 mol % 4VP. This may be related to the differences in the glass-transition temperatures of the polymers (for PEA and PMMA, ca. -11 and 126°C, respectively, by DSC).

### IR spectroscopy studies

As in other ionomer blends studied in this laboratory,<sup>16–19,25</sup> the miscibility enhancement in this system



**Figure 2** FTIR spectrum of a blend of SØPTØØ-Acid and PMMA-4VP. The reference spectrum is the addition of the individual spectra of the two homopolymers under the same conditions and so represents the unreacted SØPTØØ-Acid/PMMA-4VP blend.

was expected to be a result of a proton transfer from the sulfonic acid group to the 4VP ring. This was confirmed by IR spectroscopy studies. The pyridine group in the PMMA-4VP component exhibits an IR absorption band at  $1416\text{ cm}^{-1}$  corresponding to the in-plane C—C ring vibrations. Upon quaternization of the nitrogen atom in the pyridine ring, the ring becomes more compact because of the positive charge on the nitrogen. Consequently, the net length of the C—C bonds in the ring becomes smaller, and a new IR band appears at  $1642\text{ cm}^{-1}$  that corresponds to the in-plane stretching vibration of the aromatic ring of the ionic 4-vinyl pyridinium groups. Therefore, the decrease in

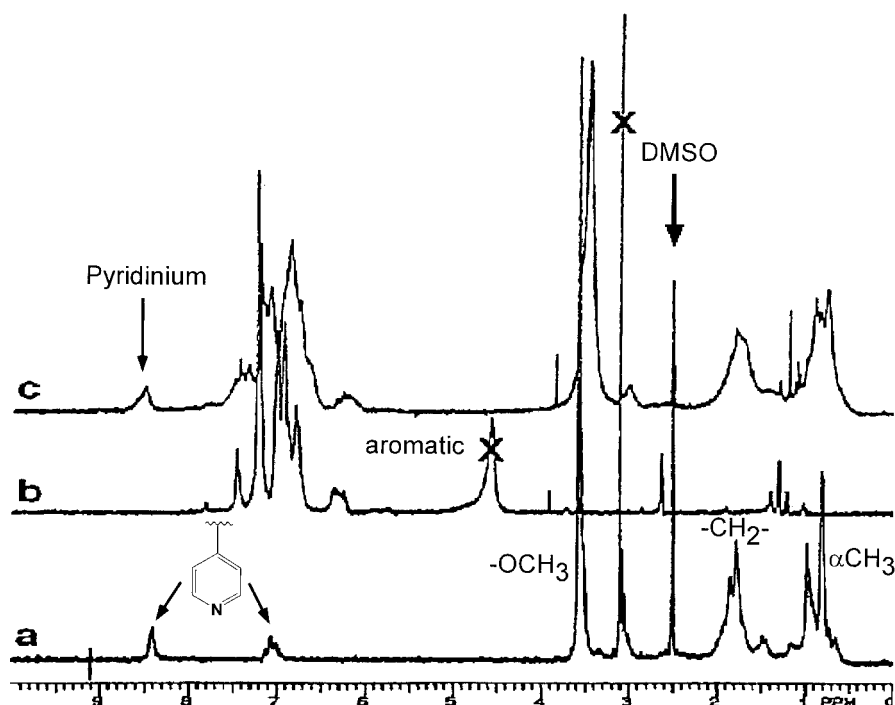
the intensity of the  $1416\text{-cm}^{-1}$  band of 4VP and the parallel increase in the  $1642\text{-cm}^{-1}$  band indicate the quaternization of the nitrogen atom. Figure 2 shows the IR spectrum of the blend in the region of interest. The small band at  $1416\text{ cm}^{-1}$  and the large band at  $1642\text{ cm}^{-1}$  show that the proton-transfer process is extensive. A semiquantitative analysis was based on the  $1739\text{-cm}^{-1}$  C=O stretching band of PMMA as the internal standard. The ratio between the intensity of the  $1416\text{-cm}^{-1}$  pyridine band of PMMA-4VP and the  $1739\text{-cm}^{-1}$  C=O band of PMMA remains unchanged in an unreacted polymer, as long as the level of the ionic group substitution in the polymer is constant. A decrease in this ratio indicates a decrease in the concentration of the 4VP moiety in the polymer due to the transfer of the proton from the  $\text{SO}_3\text{H}$  group to the pyridine group, which forms the 4VPH<sup>+</sup> cationic group:

$$\% \text{ Conversion} = \frac{\left(\frac{A_{1416}}{A_{1739}}\right)_{t=0} - \left(\frac{A_{1416}}{A_{1739}}\right)_{t=\tau}}{\left(\frac{A_{1416}}{A_{1739}}\right)_{t=0}} \times 100 \quad (1)$$

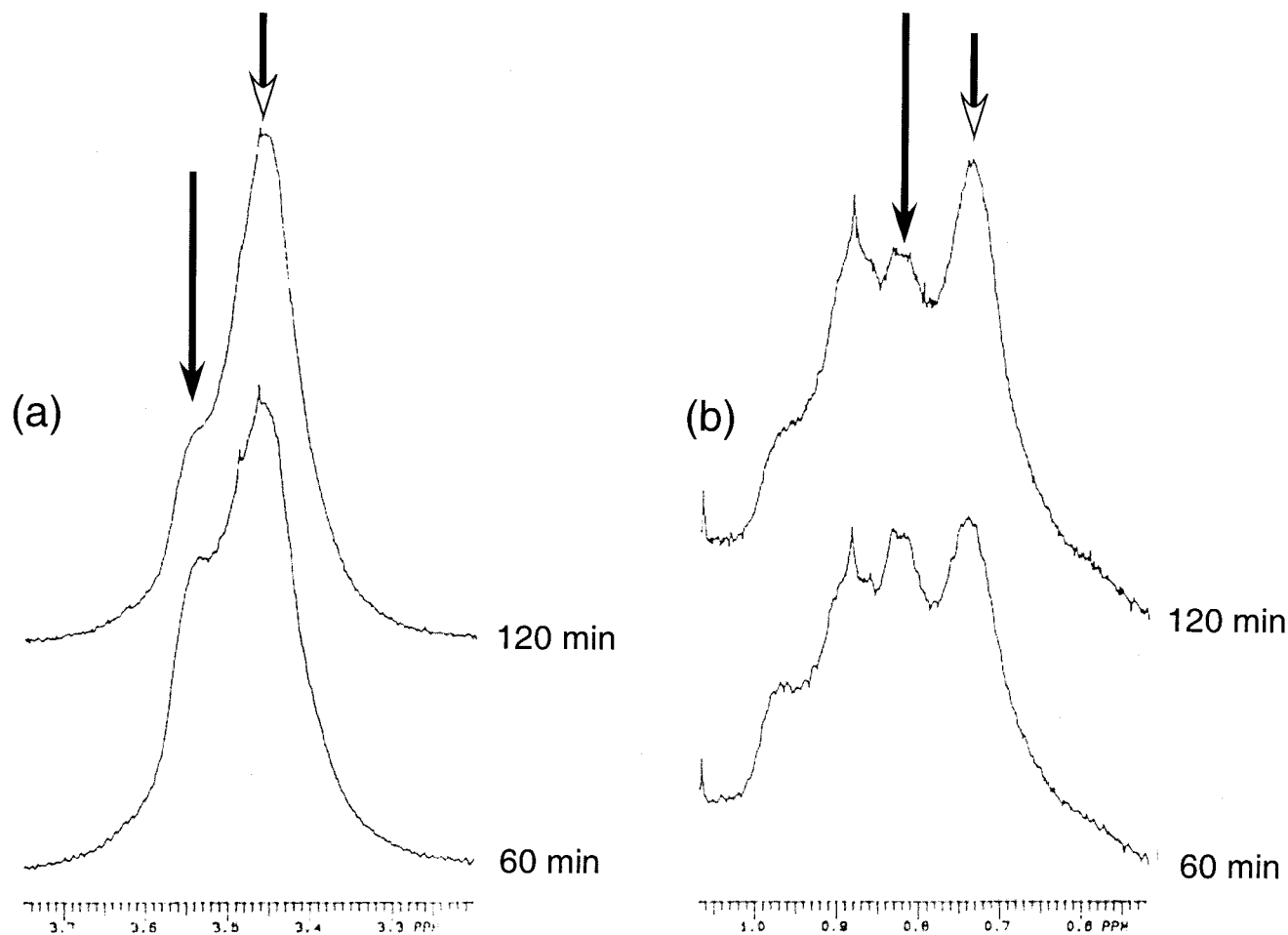
where  $A$  denotes the absorption at a given wavenumber. With this analysis, it is possible to assess that 72% of the 4VP groups are subjected to proton transfer.

### NMR studies

Figure 3 presents the NMR spectra of the blend and the two separate components, PMMA-4VP and



**Figure 3** H-NMR spectra of (a) PMMA-4VP, (b) SØPTØØ-Acid, and (c) a blend of the two registered in  $\text{DMSO-}d_6$  at  $90^\circ\text{C}$ . X = traces of water; ↓ = DMSO signal.



**Figure 4** H-NMR spectra of blends registered during the mixing process: (a) methoxy signal and (b)  $\alpha$ -methyl signal.

SØPTØO-Acid. The spectrum of the blend was obtained after the system reached equilibrium at 90°C, that is, after about 2 h. The main change in the proton spectrum of the blend, in comparison with the spectra of the components, is the shift downfield of the signal belonging to the pyridine aromatic protons ortho to the nitrogen. As discussed previously, this means that a positive charge appeared on the nitrogen (the pyridine became a pyridinium ion). Another change, more difficult to observe, is the slight shift upfield (ca. 0.08 ppm) of most of the signals belonging to PMMA-4VP. This kind of shift was observed previously on another similar blend, that is, PMMA-4VP with poly(styrene-*co*-styrene sulfonic acid) (PS-SSA).<sup>23</sup>

Figure 4 presents the signals for the methoxy and  $\alpha$ -methyl protons after 1 and 2 h. There is a change in the relative peak height of the two paired peaks indicated by arrows. The resonance peaks marked with a heavy arrow occur at the same position as the corresponding peaks in pure PMMA. Their intensity decreases with time in favor of the peaks marked with a light arrow, which are shifted upfield. This upfield shift can be explained in the same way as the shift appearing in the blend of PMMA-4VP with PS-SSA,<sup>23</sup>

that is, by a shielding effect of the aromatic rings in sulfonated polyphenylene on the PMMA-4VP protons. This shielding effect appears in the blend because of the interpenetration of the two different chains; this is a slow process. When equilibrium is reached, most of the MMA chains are aligned with the aromatic chains at such a small distance as to create an average shielding of 0.08 ppm. This is a slightly bigger distance than in the previous case,<sup>23</sup> but the experiment was carried out at 90°C rather than 85°C, which was used for the blend of PMMA-4VP with PS-SSA. Also, the different molecular geometry of the aromatic system must be considered.

To obtain another estimate of the intermolecular distance in the blend, we performed a nuclear Overhauser and exchange spectroscopy (NOESY) experiment, but no cross peaks were observed between the two polymers. This suggests that the intermolecular distance has to be greater than 4 Å.<sup>29,30</sup> Also, in this system, traces of water were present, which might have prevented the efficient alignment of the two types of chains. A kinetic study that would determine which factors are decisive in this coil overlap process is in progress with a PMMA-4VP/PS-SSA blend.

## CONCLUSIONS

A high degree of miscibility between SØPTØO-Acid and PMMA-4VP is evident from a single drop in the  $G'$  curve. IR spectroscopy studies in bulk confirm the presence of ionic interactions due to proton transfer from the sulfonic acid to the 4VP ring. From NMR studies in DMSO, we have found that the methoxy and  $\alpha$ -methyl signals initially resonate at the same frequency as for pure PMMA-4VP, but those initial signals diminish in time, and new upfield signals appear and grow. This upfield shift is due to a shielding effect of the aromatic rings in SØPTØO-Acid on the PMMA-4VP protons. No cross peaks were observed in an NOESY experiment between the polymers, and this suggests that the intermolecular distance between the chains has to be larger than 4 Å.

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