

Apparent Low-Field Microwave Absorption Properties of Styrene-Based Copolymers Containing Acid Groups

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ABSTRACT: The microwave absorption properties of polystyrene (PS) copolymers containing sulfonic and methacrylic acid groups were investigated using an electron magnetic resonance spectroscopy method. It was found that, unlike PS and poly(methyl methacrylate) homopolymers, the acid groups containing PS copolymers showed three electromagnetic resonance signals at 3250, 3035, and 520 G; the first and last two signals were thought to be due to the presence of anion radicals and acid groups in PS, respectively. This result indicated that the PS copolymers exhibited magnetic field dependent low-field microwave absorption behavior. This also suggested that the

low-field microwave absorption required the presence of both the aromatic and acidic groups in the materials. To explain both the low-field absorption and magnetic field dependence, we proposed a coupled mechanism including both the magnetoplasticity associated with a plastic deformation and the rotational degree of freedom of aromatic groups containing electric dipoles with natural spin defects. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3355–3359, 2008

Key words: microwave absorption; electron magnetic resonance (EMR); styrene copolymer; magnetoplasticity

INTRODUCTION

As much as the application of the electromagnetic (EM) waves to communication devices becomes ubiquitous, the ways of their effective shielding attracts much attention to prevent possible health hazards. While some conductive materials have been used for the EM shielding,^{1–6} their poor optical transparency gravely limits the manipulation of diverse colors. Therefore, highly wanted are materials that have both the EM shielding properties and the optical transparency. Very recently, it has been reported that optically transparent polymeric materials could absorb the energy in the range of microwave frequencies when they have nonvanishing electric dipoles consisting of anionic dopants and aromatic cations in side chains.⁷ In principle, these microwave absorption could be understood in the context of the fluctuation-dissipation theory. Under the external microwave electric field, the motions of the electric dipoles change from random thermal fluctuations to forced oscillations, synchronizing with the microwave frequencies; thus, the polymers absorb the microwave energies.

From a chemical point of view, similar microwave absorption mentioned above could also be found in various ion-containing polymers as some of them contain cationic dopants and anionic groups attached to the polymer backbone chain.⁸ For the last two decades, our group has studied the mechanical properties and morphology of polystyrene (PS)-based ionomers.^{9–14} Very recently, in the course of the investigation of the formation of free radicals in the PS-based ionomers, we observed with serendipity that the PS ionomers had the microwave absorption property.¹⁵ Thus, we thought that the PS-based ionomers were the most promising candidates for the microwave absorption study; their chemical structures somewhat resemble those of the “poly (ionic liquid)”. Therefore, we decided to carry out a more systematic study on the microwave absorption. Prior to the study on the microwave absorption property of PS ionomers, we investigated the EM properties of the PS copolymers containing acidic repeat units, and in this article we proposed a reasonable mechanism of the microwave absorption behavior of the materials. The results obtained from the PS-based ionomers neutralized with various cations will be given and discussed in a separate paper.

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EXPERIMENTAL

Sample preparation

PS (M_w = ca. 580,000 MWD = ca. 1.6) was prepared by bulk free-radical polymerization using benzoyl

peroxide as the initiator. For homogeneous sulfonation, the modified method of Makowski et al. was used to obtain the poly(styrene-*co*-styrenesulfonic acid) (PSSA) sample.¹⁶ To determine the acid content, the sample was dissolved in a benzene/methanol (9/1/ v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point; the acid content was about 4.0 mol %. Poly(styrene-*co*-methacrylic acid) (PSMA) random copolymers were also prepared by free radical polymerization in bulk.⁹ To determine the acid contents, the same method mentioned above was used; the acid contents were about 3.6 and 7.1 mol %. Poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate-*co*-methacrylic acid) (PMMAMA) copolymer containing 4.0 mol % of acidic units were prepared by free-radical solution polymerization using benzoyl peroxide as the initiator and tetrahydrofuran as the solvent.¹⁷

Spectroscopy and X-ray diffraction experiments

Electromagnetic resonance (EMR) spectroscopy experiments were performed by using a Jeol JES-FA200 X-band spectrometer (9.1–9.5 GHz) (Peabody, MA). The DC magnetic field was swept from 0 to 10,000 G, and the amplitude and frequency of the AC magnetic field modulation were 5 G and 100 kHz, respectively. The receiver gain used was 5×10^2 . To measure the EMR signals of polymer samples as a function of magnetic field, each sample in powder form was sealed in the 3-mm (diameter) EMR tube under a pressure of 5×10^{-5} Torr and then placed at the center of the TE₀₁₁ cylindrical cavity, in which the oscillating microwave magnetic field was maximum in its power. To determine the amounts of transition metal elements in the polymer samples, Jobin-Yvon Ultima Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Edison, NJ) was used. The X-ray diffraction (XRD) patterns of polymer samples were recorded using a PANalytical X-ray diffractometer (X'pert PRO MPD) with a PW 3015/20 X' celerator detector (Almelo, the Netherlands). The Cu radiation ($\lambda = 0.1542$ nm) was utilized, and the power of the X-ray generator was 40 kV and 30 mA. The scanning speed was 1°/min, and the sampling width was 0.05°. For the study on the morphology of the copolymers, a scanning electron microscope (Hitachi S-4800) (Tokyo, Japan) was used with the accelerating voltage of 15 keV. The surface of the specimen was coated with Pt using an ion sputter deposition method.

RESULTS AND DISCUSSION

Figure 1 displays the EMR signals obtained from PS and PSSA containing 4.0 mol % of acidic repeat

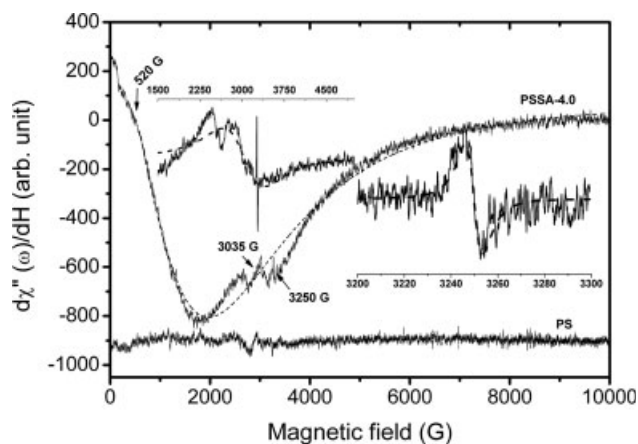


Figure 1 Electron magnetic resonance signals for PS homopolymer and PSSA-4.0 copolymer, measured at room temperature. Curves displaced vertically for clarity.

units (PSSA-4.0). It is seen that the PS shows only a very small signal at 3000 G, which is attributed to an instrumental background. In the case of the PSSA-4.0 copolymer, three EMR signals are observed; i.e. the first and very small signal at 3250 G and the second signal centered at 3035 G with a medium line-width and intensity (here, the source of an anomalously resolved fine structure would be the same as that of the PS), and the third signal, a very large and broad signal, starting from zero magnetic field. It is seen that the three signals can be fitted with single Lorentzian functions reasonably well, with a full width at half maximum (ΔH_{fwhm}) and a spectroscopic splitting factor g ($= h\nu/\mu_B H_{\text{res}}$, where h = Planck constant, ν = microwave frequency, μ_B = Bohr magneton, H_{res} = resonant magnetic field) for each signal as follows: For the first signal (see the lower-right inset of Fig. 1), ΔH_{fwhm} and g are 12.8 ± 0.2 G and 2.003, respectively, for the second (the upper-left inset), they are 1260 ± 11 G and 2.147, respectively, and for the third, the values are 5182 ± 12 G and 13.77, respectively. At this point, it should be mentioned that the signals in the upper-left inset of Figure 1 was regenerated after the subtraction of the Lorentzian function used for the fitting of the third EMR signal from the raw data. In addition, the successful fitting of the signals with the Lorentzian functions indicates that the spin entities in three different environments are in weak collision limits ($\omega\tau_c \ll 1$) with correlation times, $\tau_c < 1/\omega$ ($\omega = 2\pi\nu$). These fast motions may be related either to molecular thermal motions or to phonon modes that could affect the motions of paramagnetic spins of polymers strongly.

Now let us discuss the sources of the signals. According to the work by Golovin and Morgunov, the EMR signal at 3250 G ($g = 2.003$) is due to the presence of SO_3^\bullet radicals of the PSSA with ΔH_{fwhm}

= 10 G.¹⁸ In the case of other two major signals at 520 and 3035 G ($g = 13.77$ and 2.147 , respectively), however, the source of the signals has not been identified yet. Nevertheless, one can intuitively postulate that these two signals must be related to the presence of the sulfonic acid groups in the PSSA because the PS homopolymer does not show these two signals. To verify this postulation, we prepared another PS-based copolymers containing carboxylic acid groups, instead of the sulfonic acid groups, i.e. PSMA copolymers, and then performed the EMR measurement of the PSMA copolymers under the same experimental condition for the PSSA system. The EMR results are shown in Figure 2. Interestingly enough, the PSMA copolymers containing 3.6 and 7.1 mol % of acidic repeat units also show a very broad EMR signal at low magnetic fields and a medium-sized signal at 3035 G. The PSMA copolymers also exhibit a relatively weak EMR signal at 3245 G. Since the position of the signal at 3245 G is similar to that of the sulfonic acid radical of the PSSA (i.e. 3250 G), it can be suggested that this signal is also due to the presence of the carboxylic acid radicals. In addition, it is observed that the intensities of the broad signals at 520 and 3035 G ($g = 13.7$ and 2.147 , respectively) increase with increasing amounts of acid groups.

Since the EMR results of PS are different from those of the PSSA and PSMA copolymers, it would be useful to see whether the morphologies of the polymers are responsible for the difference or not. Figure 3 shows the SEM images of PS, PSSA-4.0, and PSMA-3.6 polymers. It is seen that the SEM images of the three polymers are almost identical. This indicates that the morphologies of the samples in nanometer scales are not related to the difference in the EMR signals.

At this point, one question arises. To have the low-field microwave absorption, do the polymers

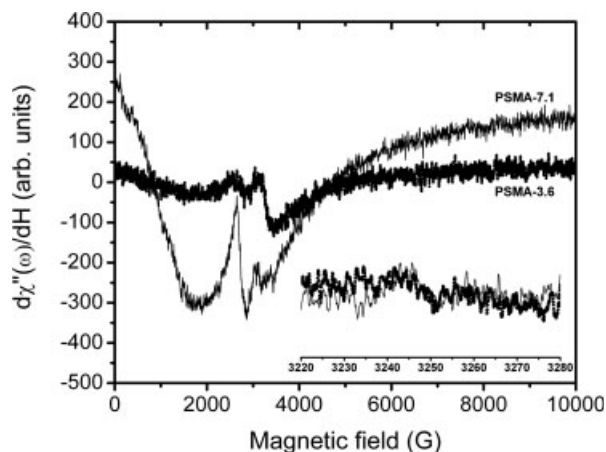


Figure 2 Electron magnetic resonance signals obtained for PSMA-3.6 and PSMA-7.1 copolymers, measured at room temperature. Curves displaced vertically for clarity.

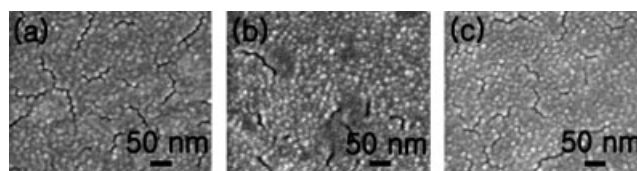


Figure 3 Scanning electron microscope images of (a) PS homopolymer, (b) PSSA-4.0 copolymer, and (c) PSMA-3.6 copolymer ($\times 100,000$ magnification).

need to contain the aromatic moiety and acid groups together or only the acid groups in the polymer matrix? To answer this question, we prepared poly(methyl methacrylate) (PMMA) and its copolymer containing 4.0 mol % of acidic units, i.e. poly(methyl methacrylate-*co*-methacrylic acid) (PMMAMA-4.0). The PMMA and PMMAMA-4.0 do not have any aromatic moiety in the polymer chains. No EMR signal is observed for the PMMA and PMMAMA-4.0 (see Fig. 4). This result indicates that the two signals at 520 and 3035 G appear only for the copolymers containing both the aromatic and acid groups and that the interactions between the aromatic and acid groups play an important role in inducing the two broad EMR signals. The increasing intensity of the broad EMR signals with increasing acid contents, shown in Figure 2, is also in good accordance with the above interpretation, i.e. the more ionic groups, the more interactions between the aromatic and acid groups, and the higher intensity of the EMR signal.

Let us discuss the microwave absorption at a low magnetic field. To the best of our knowledge, the low-field microwave absorption can be originated from a ferromagnetic resonance and electric dipole transitions. Firstly, the microwave absorption can be induced by the ferromagnetic resonance due to the presence of the clusters or complexes of transition metal elements that might be accidentally

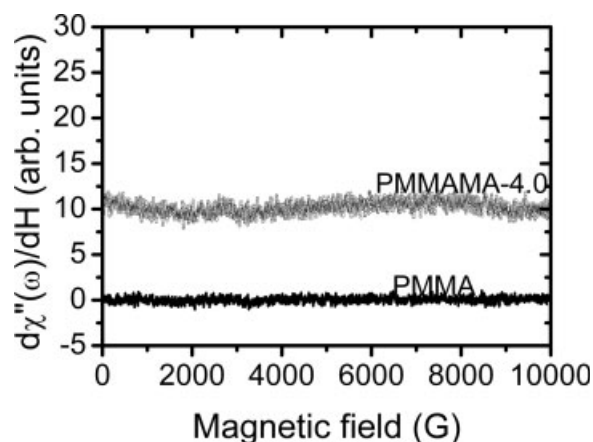


Figure 4 Electron magnetic resonance signals for PMMA homopolymer and PMMAMA-4.0 copolymer, measured at room temperature. Curves displaced vertically for clarity.

incorporated with copolymers during the sample preparation. If the clustered impurities or complexes of the transition metal elements existed in the sample, the material would show the absorption caused by the ferromagnetic resonance. At this point, it should be mentioned that the ICP-AES and XRD methods are appropriate methods to detect the impurities of various transition metal elements in the materials and the complexes containing transition metal elements, which have their own crystalline structures, respectively. Thus, we checked the possibility of the presence of the impurities and complexes of transition metal elements using the methods mentioned above. The ICP-AES results are listed in Table I, and the XRD patterns are shown in Figure 5. It is seen that the amounts of the transition metal impurities in the PS copolymers are smaller than those in the PS homopolymer. This indicates that the presence of impurities cannot be responsible for the strong low-field microwave absorption. In addition, the XRD patterns show peaks, related to only amorphous PS copolymers, implying the absence of the transition metal complexes. Furthermore, if the transition metal impurities caused the low-field microwave absorption, the intensity of the absorption peak should be different from sample to sample because each sample would have varying and uncontrollable amounts of impurities. This is not the case here because the apparent low-field microwave absorption is observed only for the PS-based copolymers and also the intensities of the EMR signals change systematically with the acid contents. Thus, the low-field microwave absorption cannot be explained by the ferromagnetism. As far as the electric dipole transitions as the cause of the absorption are concerned, we should take into account nonresonant microwave absorption. The nonresonant microwave absorption is attributed to the electric dipole transitions between the quantized energy levels established by the rotational degree of freedom of various dipoles of the polymer chains. Recently, the same concept has been used to explain the finite microwave absorption of some poly(ionic liquid)s.⁷ Thus, this concept could also be applicable to the zero-field microwave absorption of our system.

TABLE I
ICP-AES Data of PS, PSSA, and PSMA Copolymers

Samples	Amounts of transition metal impurities (ppm)		
	Fe	Cu	Mn
PS	0.281	0.018	<0.01
PSSA-4.0	0.127	0.064	<0.01
PSMA-3.6	0.177	0.021	<0.01
PSMA-7.1	0.149	0.018	<0.01

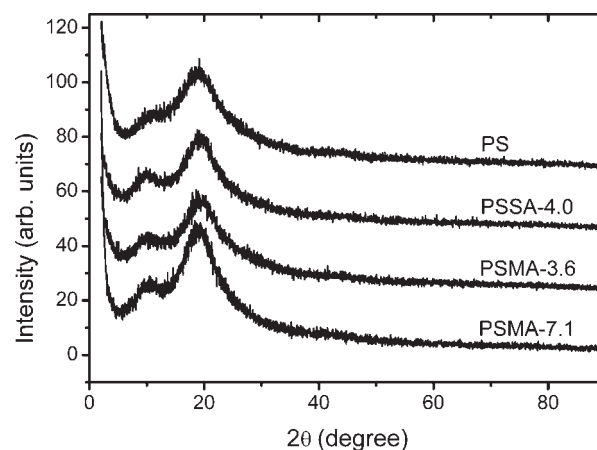


Figure 5 XRD patterns of PS, PSSA, and PSMA polymers. Curves displaced vertically for clarity.

Even though the concept of the electric dipole transitions can explain the zero-field microwave absorption, it cannot be applicable to the explanation of the magnetic field dependence of the absorption. At this point, it is worth recalling that a “magnetoplasticity” associated with the plastic deformations of PS under a static magnetic field together with the irradiations of an alternating microwave frequency was reported by Golovin and Morgunov.¹⁸ They interpreted that the magnetoplasticity was due to the coupling of the defect spin states and the vibrational degree of freedom of the pendent groups of the PS. Here, the static magnetic field and the oscillating microwave frequency were known to contribute to the splitting of spin degeneracy and the manipulation of spin populations at the splitting energy states, respectively. In this regime, the vibrational energy of aromatic groups can be exchanged with the Zeeman splitting energy of natural spin defects. Unfortunately, however, the magnetoplasticity itself cannot be used to explain the low-field microwave absorption, because the PS and PMMA do not show any low-field microwave absorption. Thus, we propose a coupled mechanism to explain the findings in the present work, which should include both the electric dipole transitions causing the low-field microwave absorption and the magnetoplasticity for the magnetic field dependence. If the electric dipoles are introduced to PS, the microwave absorption at zero magnetic field caused by the rotational degree of freedom of the aromatic and anionic groups can be observed. Simultaneously, the magnetoplasticity due to the vibrational modes of the aromatic groups containing electric dipoles with spin defects should also be observed in the wide magnetic field range. Here, the aromatic groups play a key role in the microwave absorption and its field dependence. Since the averaged rotational motions of the aromatic groups make a contribution to the

overall microwave absorption, the microwave absorption is expected to take place over a wide range of magnetic field. These, mentioned above, are indeed what we observed here.

CONCLUSIONS

In summary, we found for the first time that the acid-containing PS copolymers had microwave absorption properties. In addition, we also demonstrated that such absorption phenomena were affected by the applied magnetic field, i.e. field dependence. To explain the magnetic field-dependent low-field microwave absorption, we suggested a coupled mechanism including the concept of the rotational degree of freedom of the aromatic groups with spin defects for the low-field microwave absorption and the magnetoplasticity concept for the field dependence. As known, the PS-based ionomers are one of the few polymeric materials used in common purposes and have optical transparency.⁸ Thus, we have expanded our research area into the PS-based ionomers having the field-dependent microwave absorption property. The study on the PS ionomers neutralized with various cations will be published soon. In addition, we plan to investigate the microwave absorption properties of another transparent polymeric materials containing aromatic groups and electric dipoles with spin defects.

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