Ultrafine Metal Particles in Polymers and the Formation of Periodic Polymer Stripes

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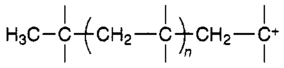
Received July 14, 1995
Revised Manuscript Received September 14, 1995

The ability to design new composite materials consisting of polymer insulators and metals is currently an important driving force in many aspects of materials and polymer research.[1−5] The properties of these materials can be tailored by altering the metal particles, their size and shape distributions, or their relative concentrations. Current methods for the preparation of polymer/metal composites are generally focused on plasma polymer thin films and include simultaneous plasma etching and plasma polymerization,[6,7] simultaneous evaporation of polymer and metal from separate sources, or simultaneous plasma polymerization and metal evaporation from high-temperature crucibles.[8−10] The combination of laser vaporization/ionization of metals with the very fast propagation rates characteristic of ionic polymerization offers great promise and advantages in this regard. The potential advantages of laser vaporization include less complicated processing, solvent-free environment, variable metal vapor flux depending on the laser power, and sequential or simultaneous evaporation of several metals or metal oxides. Here we present the results of an investigation of a new method for cationic polymerization of bulk liquid monomers that leads to the incorporation of ultrafine metal particles into polymer matrices. In this study we were able to encapsulate ultrafine metal particles in a polyisobutylene (PIB) matrix and to form periodic PIB stripes. Such composite materials could find use in a variety of applications that depend on conductivity and magnetism.

The method described here is related to our work on metal ion catalyzed polymerization in the gas phase,[11,12] within gas phase clusters of the monomer molecules,[13,14] and in the bulk liquid monomer.[15,16] In the present experiments, the monomer liquid is placed in a glass vessel inside a vacuum chamber and the temperature is controlled by circulating liquid N_2 or other appropriate coolants through copper coils wrapped around the glass vessel. Pulsed-laser vaporization is used to generate energetic metal ions from a metal target placed above the monomer liquid. The laser vaporization method typically releases more than 10^{14} metal atoms and about 10^5 metal ions per pulse (20 ns pulse width). In addition, fast electrons capable of ionizing the monomer molecules are also produced. We used the second harmonic of a Nd:YAG laser (532 nm) operating at 10 Hz with an average power of 10−30 mJ/pulse. The laser light was slightly focused on a 1−2 mm^2 area of the metal target using a 30 cm focal length lens. Isobutylene was chosen as an appropriate monomer for a prototype study since it is known to be polymerized in the bulk liquid by only cationic mechanisms.[17] The temperature of the monomer was kept between −120 and −140 °C, and the pressure ranged from 10^{-3} to 10^{-1} Torr by using either He or Ar as a carrier gas. Several metal targets such as Zn, Ti, Zr, Fe, Al, Sn, Pd, and Pt were used. Under typical experimental conditions, the generated ions undergo several collisions with the monomer molecules in the gas phase which result in a variety of bimolecular ion−molecule reactions. The product ions from these reactions are pulled into the monomer liquid by applying an electric field (100 V/cm) between the metal target and the bottom of the liquid cell.

Considerable insight into the mechanism of this polymerization and the gas phase reactions occurring in the early stages of the process can be gained by using laser vaporization high-pressure mass spectometry (LVHPMS) as recently reported.[11,12] In these experiments, laser vaporization of a metal target takes place inside a HPMS source which contains a mixture of isobutylene/carrier gas (Ar or N_2) at selected pressures typically in the range of 0.01−2 Torr. Although the atomic metal cations were generated in all cases as indicated from the mass spectra, the metal cations were not directly observed in the case of Zn due to a charge transfer reaction to isobutylene generating the $C_4H_8^+$ ions. This is consistent with the ionization potential (IP) of Zn (9.4 eV), which is higher than that of isobutylene (9.2 eV).[18] For other metal atoms with IP's lower than isobutylene such as Ti, Zr, and Pt, dehydrogenation reactions and the formation of metal−C_4H_x ($x<6$) adduct ions were observed. In all cases, the *tert*-butyl carbocation, $C_4H_9^+$, was observed with a significant intensity. This carbocation is known to be the active initiator for isobutylene cationic propagation in bulk liquid, which proceeds according to.[17,19]



$$H_3C-C-(CH_2-C)_n-CH_2-C^+$$

The most interesting finding from the LVHPMS results is the evidence that the initiation reaction producing the $C_4H_9^+$ ion and the first few steps of its sequential additions can take place in the gas phase under typical conditions of our liquid polymerization experiment.

Following the laser vaporization for 40−60 min, the reaction cell is allowed to come to room temperature while the unreacted monomer evaporates, leaving the product polymers. The polymers are usually collected on glass substrates for microscopic analysis. The images obtained by SEM indicate that the spherical metal particles are present within the polymer matrix. Most of the metal particles are in the size range of 100−200 nm. (Figure 1a). However, few particles in the micron size range are also present (Figure 1b,c). In our experiments the parameters controlling particle growth are the temperature of the reaction system and the flux of metal vapor generated by the laser vaporization, the former determining the mobility and the latter the growth velocity. The amount of metal particles in the polymer matrix can be increased by increasing the laser power, which increases the metal vapor flux. However, this also leads to larger particles and we attribute this behavior to the particle's coalescence in the matrix (Figure 1b). Evidence for polymer formation on the large surface areas of the Zn particles is clearly seen in Figure 1c. The polymer formed on the particles' surfaces exhibits a spherulitic morphology. Atomic force microscopy has indicated that metal particles are present above and below the surface of the polymer film. We have found that laser vaporization of Zn gives the highest polymer yield as compared to the other metals used. This is attributed to the efficient ionization of isobutylene through the charge transfer reaction from

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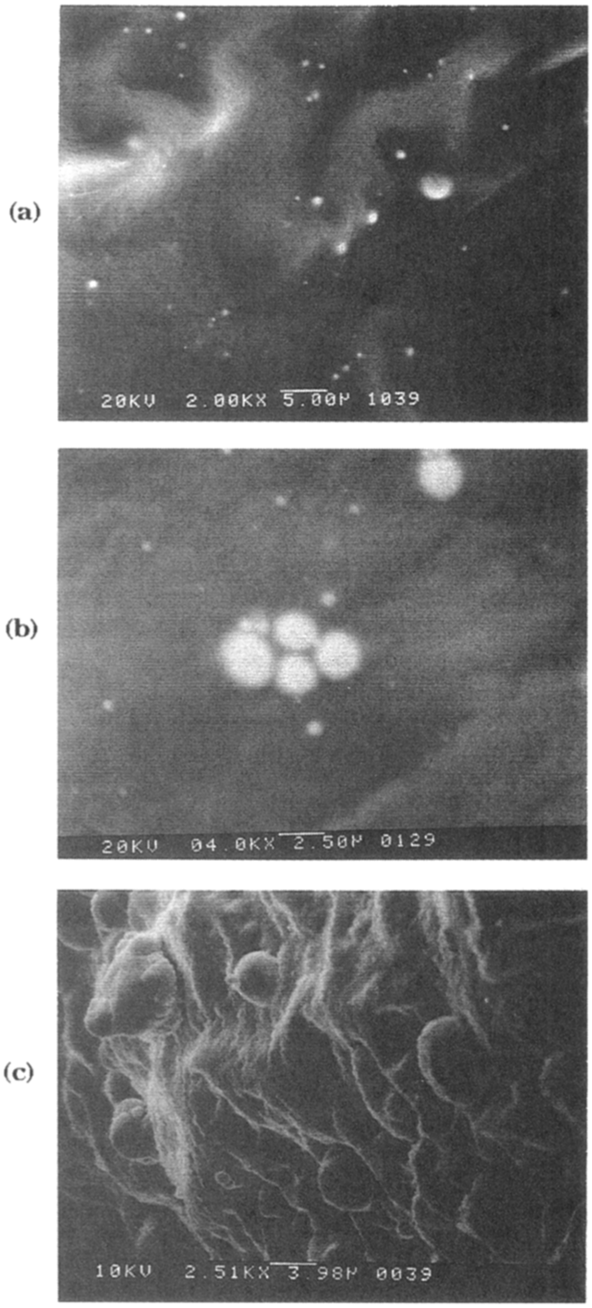

Figure 1. SEM micrographs of polyisobutylene film containing (a) Cu particles and (b) a cluster of large Ni particles. (c) Polymer growing on Zn particles.

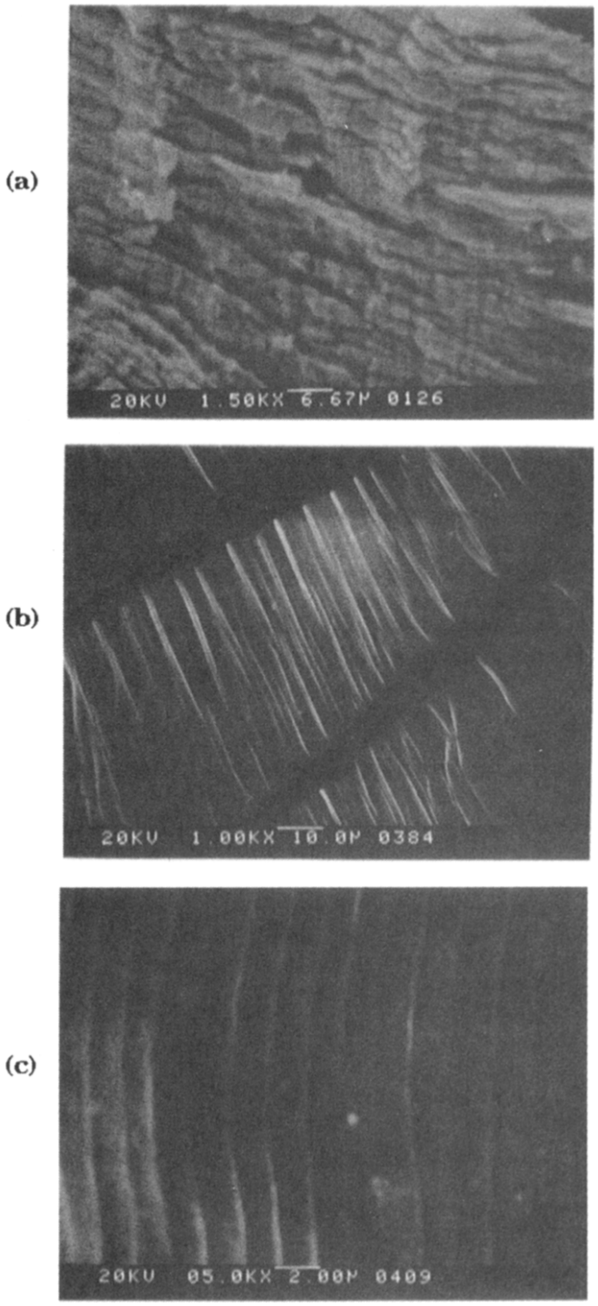

Figure 2. SEM micrographs of polyisobutylene films obtained in the presence of an electric field: (a) thick polymer deposit with 500 V/cm field; (b) thin polymer film with 800 V/cm field; (c) higher magnification of image (b).

Zn^+. The average molecular weights (M_w) of the polymers depend on the duration of the experiment, and values as high as 1×10^6 ($M_w/M_n = 4-5$, depending on the experimental conditions) were determined by the GPC method (with polystyrene standards).[20]

A striking feature of this polymer is the modulation of the morphology by applying an electric field within the monomer liquid. Two copper electrodes were immersed in the liquid monomer, and an electric field of 500 V/cm was applied during the laser polymerization experiment (60 min) and also during the evaporation of the excess monomer after stopping the laser. Macroscopic polymer wires (threads) could be observed visually as they tended to stretch from one eletrode to the other. As shown in Figure 2a the resulting polymers exhibit macroscopic patterns or textures with clear visible lamellae having periodicity in the micron size range. The polymer–metal composite preferentially nucleates and grows as stripes. By carrying out the experiment only for 10–15 min, a relatively thin polymer deposit is obtained (Figure 2b). In this case, a more symmetric array of polymer wires can be produced (Figure 2c). A high electric field (500–800 V/cm) appears to be necessary to form such structures, but less ordered arrays could also be produced by a relatively weak field (100 V/cm). The stripes are also observed within a fractured surface, suggesting that they are formed as part of the film and not only on the surface. The origin of these surprisingly periodic stripes is not yet completely clear. However, we note that the stripe morphology is known to arise in Langmuir films,[21] in thin films of magnetic garnets, and in ferrofluids. The periodic spatial organization in these systems is attributed to the presence of competing interactions and can be tuned by varying parameters such as temperature and applied magnetic, electric, or other fields.

It is postulated that the inhomogeneous electric field induces electrostatic interactions among the polarized polymer chains. This phenomenon is known as mutual dielectrophoresis and is frequently seen in dispersions of higher dielectric constant particles in a lower dielectric constant fluid.[22–24] In the current situation, there is also an additional electrostatic component because the polymer propagating ends are cationic. Therefore, we associate two different mechanisms with the patterns we have observed: the former is related to the polymer polarizability (dielectrophoresis) and the latter to the alignment of the cationic chains in the presence of the field.

We have described a class of polymer–metal composites consisting of ultrafine metal particles embedded in a polyisobutylene film. It is worth noting that the laser vaporization/polymerization method provides the ability to encapsulate several different metals or metal oxides, which undoubtedly will play a significant role in tuning the various properties of the polymer composites. The extra flexibility introduced by applying an electric field to modulate the polymer morphology makes these composites interesting candidates to explore new conducting, superconducting, or magnetic materials. Manufacturing polymers with these properties could enhance the overall electro-optic performance and the efficient use of available materials. Systematic experimentation on a range of important monomers that can be polymerized by cationic mechanisms and matched doped metals would make available a base of results upon which the properties of future polymeric materials could be reliably assessed. Further experiments using these composite materials are in progress in our laboratory.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 9311643) and the Petroleum Research Fund, administered by the American Chemical Society (2764-AC6).

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(20) The IR spectrum shows a strong peak in the 1250–1200 cm^{-1} region due to skeletal vibrations of the $C(CH_3)_2$ group and a doublet in the 1400–1350 cm^{-1} region due to in-phase and out-of-phase symmetric CH_3 deformation. The proton NMR of the polymer shows two main peaks at $\delta = 1.1$ and 1.4 with an intensity ratio of 3:1, which is consistent with the ratio of CH_3/CH_2 protons in the repeating unit $(-CH_2C(CH_3)_2-)_n$. Therefore, both the IR and NMR spectra are consistent with polyisobutylene polymers.
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MA9510202