Novel Approach to Cationic Polymerization Using Pulsed-Laser Vaporization/Ionization of Metals

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The development of new techniques for cationic polymerization is of considerable interest in a number of fundamental scientific disciplines as well as for practical applications. Under normal circumstances, ionic polymerizations are conducted with condensed systems (monomer liquid or in solution) where multiple reactions (initiation, propagation, chain transfer, termination, etc.) can occur simultaneously. Information regarding the exact nature of each mechanistic step and an understanding of the events occurring in the course of polymerization remain largely unavailable. In solution the problem is further complicated by reactions with the solvent. Under these conditions, propagation may not be due to free ions but to the cationic partner of an ion pair. The propagation rate constants for free ions are greater than those for an ion pair.[1]

In order to achieve a clearer understanding of these processes, it is desirable to examine cationic polymerizations initiated only by free ions without complications from counterions and solvents. Studies using radiation-induced polymerization have shown that under rigorous anhydrous conditions the polymerization proceeds mainly by free ions.[2,3] However, under high-energy radiation, free radicals are often produced in greater concentrations than free ions.[1] Another approach to studying polymerization by free ions involved vacuum ultraviolet (VUV) radiation;[4,5] however, there are difficulties associated with handling high-energy and VUV radiations as well as the possibility of damage to the polymer. It is therefore valuable to explore new techniques to initiate free ion polymerization to obtain more explicit data.

In this paper, we report the discovery of a novel technique to initiate cationic polymerization using pulsed-laser vaporization/ionization of metals. This discovery was made during our recent observations of consecutive addition and elimination reactions following the encounter of Ti^+ with gas-phase clusters of isobutylene.[6] These observations suggest that the injection of energetic metal ions into liquid monomers may initiate polymerization. Specifically, we report herein the applicability of this technique to the synthesis of polyisobutylene polymers with average molecular weights (M_w) greater than 1×10^6. Isobutylene is known to be polymerized in the liquid phase only by cationic mechanisms,[1] and therefore a successful polymerization would provide direct evidence for the mechanism involved. Significantly, in addition to the synthesis of high molecular weight polymers, the technique described here has potential applicability to the synthesis of metal-doped polymer films. We intend to show that this can be achieved through the incorporation of ultrafine metal particles and clusters in the polymer matrices as it is formed.

In our experiments, energetic metal ions were generated by pulsed-laser vaporization of a metal target placed above the monomer liquid inside a vacuum chamber. The monomer liquid (isobutylene, 99% Aldrich) was placed inside a glass vessel, and the temperature was controlled by circulating liquid N_2 or other appropriate coolants through copper coils wrapped around the glass vessel. The liquid was stirred with a Teflon-coated magnet, and the target metal rod was placed about 2–3 cm above the liquid surface. The results presented here were obtained by laser vaporization of the metals Ti, Zr, and Sn using the second harmonic of a Nd:YAG laser (532 nm). The laser was operated at 5 Hz with an average power of 5–20 mJ/pulse (20-ns pulse width). The laser light was slightly focused on a 1–2 mm^2 area of the metal rod using a 30-cm focal length lens. The temperature of the monomer was kept between −100 and −120 °C, and the pressure ranged from 10^{-3} to 10^{-1} Torr. Experiments (with Ar or He as a carrier gas) showed that above 10 Torr no significant amount of solid polymer was detected. The reaction time was varied from 20–60 min. By placing the reaction vessel between two parallel metal plates and applying a potential difference of

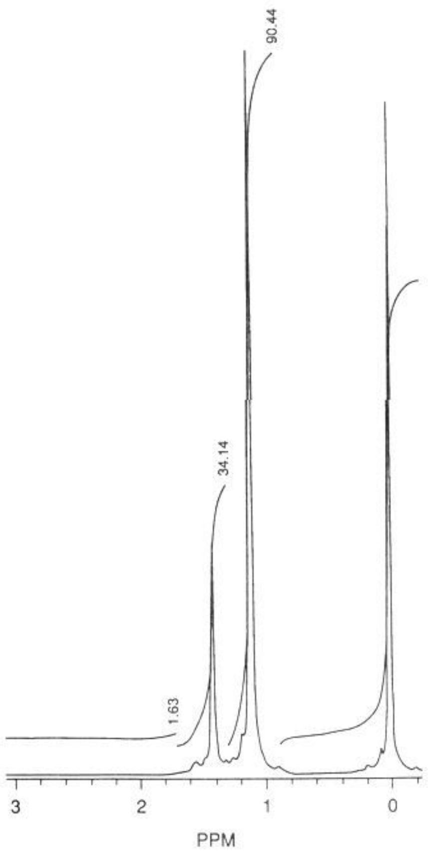

Figure 1. ^1H NMR spectrum of the polymer (in $CDCl_3$).

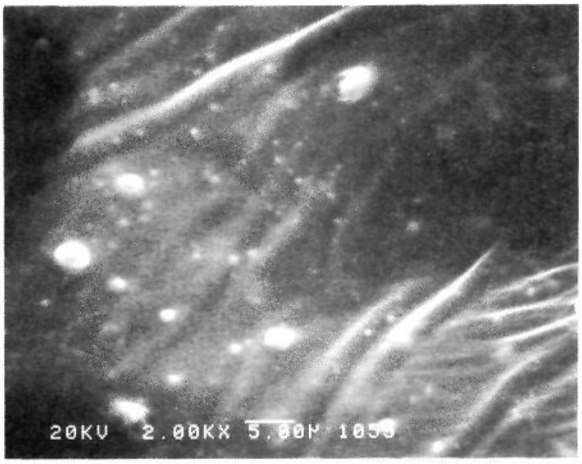

Figure 2. Electron micrograph (SEM) of polyisobutylene film containing Zr particles.

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200–500 V, the polymer yield was doubled. However, polymerization took place even in the absence of any applied field with all the metals investigated. No polymer was formed when the laser was focused on the vapor above the liquid instead of the metal target.

On the basis of the ^1H NMR spectrum of the polymer (in $CDCl_3$), shown in Figure 1, the ratio of CH_3/CH_2 protons (at $\delta = 1.1$ and 1.4, respectively) is 3:1, which is consistent with a repeating unit of the form $(-CH_2-C(CH_3)_2-)_n$. The polymer was dissolved in THF and filtered. The M_w was determined by GPC (with polystyrene standards). The GPC curves of the polymers obtained by vaporization of Sn (placed in a potential of 150 V/cm) and Zr (with no applied field) indicate a bimodal distribution. In the Sn experiment, the area ratio of the higher M_w fraction ($\sim 1 \times 10^6$, $M_w/Mn = 1.01$) to the lower one ($M_w = 5.5 \times 10^5$, M_w/M_n 1.08) is 0.96.

Shown in Figure 2 is an electron micrograph (SEM) of a polymer film obtained by vaporization of Zr. The presence of micron- and submicron-size metal particles is clearly evident. The surface morphology of the polymer films obtained is dependent on experimental conditions such as laser power, temperature, pressure, and electric field strength.

To explore the mechanism of this polymerization we investigated the reactions between metal ions produced by laser vaporization and gas-phase isobutylene clusters. The isobutylene clusters were generated by pulsed adiabatic expansion in a supersonic cluster beam apparatus.[6,7] After the encounter between the atomic metal ions and isobutylene clusters, the product ions were mass analyzed using a quadrupole mass filter. The mass spectrum contained peaks corresponding to the $C_4H_9^+(C_4H_8)_n$ sequence. It is well known that laser vaporization can generate metal ions with a very high kinetic energy.[8,9] This suggests that the isobutylene ions were formed as a consequence of excess kinetic energies and possible electronic excitations of the metal ions. The $C_4H_8^+$ ions then underwent the known ion–molecule reaction with isobutylene[10,11] to form the *tert*-butyl carbocation according to:

$$C_4H_8^+ + C_4H_8 \rightarrow C_4H_9^+ + C_4H_7$$

This would mean, therefore, that the polymerization initiator in the liquid phase is the $C_4H_9^+$ ion.

In conclusion, we have discovered that high molecular weight polyisobutylene can be synthesized using a laser vaporization technique. The method can be used to initiate polymerization by ions generated from other involatile materials such as fullerenes, refractives, semiconductors, and superconductors. The method could also provide a valuable technique for the in situ doping of ultrafine metal particles into the polymer matrices during synthesis as well as for the preparation of polymeric thin films. These new directions, which are being explored for the first time, are currently under active investigation in our laboratory.

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