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Raman and FTIR Spectroscopy of Polymerization: Bulk Polymerization of Methyl Methacrylate and Styrene

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ABSTRACT: Bulk polymerization of styrene and methyl methacrylate (MMA) was investigated by diode array Raman and FTIR spectroscopy. Conversion was followed in real time by measuring the integrated intensity of the Raman and integrated absorbance of the IR bands due to the carbon–carbon double bond. We find both diode array Raman and FTIR spectroscopy to be very convenient and powerful tools to follow the bulk polymerization process. A new and strong Raman band at 1545 cm^{-1} was observed during AIBN (azobis~~(isobutyronitrile)) initiated polymerization of MMA at 60 °C. This band existed only during the gel effect~~ period. We think it is due to a reactive free radical intermediate stabilized by conjugation and detectable due to resonance Raman enhancement. Observation of this transient phenomenon further emphasizes the usefulness of simultaneous detection of a large section of the Raman spectrum with a sensitive diode array detector.

I. Introduction

In a polymerization process there are three variables of interest: conversion, average molecular weight, and the polydispersity of the product. For a batch process, measurement of all three quite accurately is possible. For automatic control purposes, however, a rapid on-line technique is needed.

Thermal polymerization has been studied by various spectroscopic techniques: quasi-elastic light scattering,[1,2] interferometry,[3,4] NMR,[5] and recently Raman spectroscopy.[6,7] With the enormous decreases in cost of computers and diode array detectors, techniques such as Raman and FTIR spectroscopy are good candidates for on-line monitoring of polymerization.

While it is not used for commercial production, thermally initiated bulk polymerization is the main method of polymerizing dental fillers and ceramic–polymer composites, which hold promise as artificial bones. In this paper we report the results of some of our studies on bulk polymerization.

Vinyl polymerization processes involve changes in the carbon–carbon double and single bonds; thus, in theory it is a straightforward procedure to obtain the relative concentrations of the monomer and polymer from the vibrational spectra. In practice, however, one has to find bands that are only present in either the polymer or the monomer and determine their dependence on concentration and chemical environment. Long-term stability and accuracy of the IR and the Raman spectrometers are also complicating experimental problems. In order to overcome both of these problems, previous investigators of styrene polymerization[6,7] have used the intensity of the ring breathing mode of the aromatic ring at 1000 cm^{-1} as an internal reference. However, as pointed out, the intensity of this band is not the same for the monomer and polymer; thus the method requires a calibration to correct for changes in the reference band. We will show later that the internal referencing is not necessary if the spectrometers are stable.

II. Experimental Section

Pure styrene and methyl methacrylate were obtained by vacuum distillation of the inhibited monomers obtained commercially (Fisher Scientific). Freshly distilled monomer was either used immediately or stored at 0 °C for no longer than several days. All of the samples polymerized in the Raman spectrometer were flame sealed under vacuum in 5-mm-o.d. polished quartz NMR tubes. The temperature of the NMR tubes was controlled by means of a tight-fitting heated metal block with holes for the beam and the scattered light. The sample temperatures were controlled to ±1 °C and are accurate to ±3 °C.

The FTIR samples were prepared by using a Harrick temperature-controlled liquid cell with calcium fluoride windows. Due to its construction the IR cell could not be sealed under vacuum. The temperature of the IR cell was controlled to ±0.5 °C by circulating hot water through the heating jacket.

The Raman spectra were obtained with a Spex 1877 Triplemate spectrograph coupled to a Tracor Northern 1024 intensified, large-area diode array detector. This arrangement allowed simultaneous measurement of all of the Raman bands within a 1300-cm^{-1} range with a 1.3-cm^{-1} resolution. Since simultaneous detection increased the signal-to-noise ratio of our spectrometers, it was possible to obtain spectra with good S/N in as short a time as 10 ms. More importantly, the lack of moving parts enabled signal-averaging and spectral subtraction with very high wavelength accuracy (better than 0.01 cm^{-1}). The spectrometer is interfaced to a HP 9836 computer for digital signal processing such as background subtraction and Gaussian peak deconvolution. The 488.0-nm line of the argon ion laser was used as the incident light. Typical power at the sample was ~15 mW.

FTIR spectra were obtained with a Diglab FTS 20 C/E Fourier Transform IR spectrometer. A broad-band MCT detector was used for high sensitivity. Between 100 and 200 scans at 4-cm^{-1} resolution were co-added to get high S/N ratio spectra every 5 min. Extensive use of the other data processing capabilities of the FTIR were made.

III. Results and Discussion

(a) Styrene Polymerization. In order to make sure that our results were consistent with those of previous investigators,[6,7] we investigated styrene polymerization first. Chu et al.[6] and Sears et al.[7] emphasize the need for an internal reference and calibration. Their choice was the ring breathing mode of styrene at 1000 cm^{-1}. This is a very sharp and intense band, which shifts only by 2 cm^{-1} to 1002 cm^{-1} in polystyrene, and, as such, would appear to make a good internal calibration standard. The only shortcoming is the change in intensity upon polymerization. According to Sears et al.[7] the ratio of the polymer to monomer intensity is 0.42 but their data taken at 100 °C have a rather large scatter. Chu et al.[6] report a ratio of 0.59 ± 0.04 determined by curve fitting to the results of a set of measurements made with known polymer–monomer mixtures presumably at room temperature. Figure 1 shows our results for the relative intensity of this band at 130 and 160 °C as a function of conversion. From Figure 1 we see that the ratio of the polymer to monomer intensity is 0.74 ± 0.05. These significantly different results show some of the problems associated with making quantitative Raman intensity measurements when sample changing,

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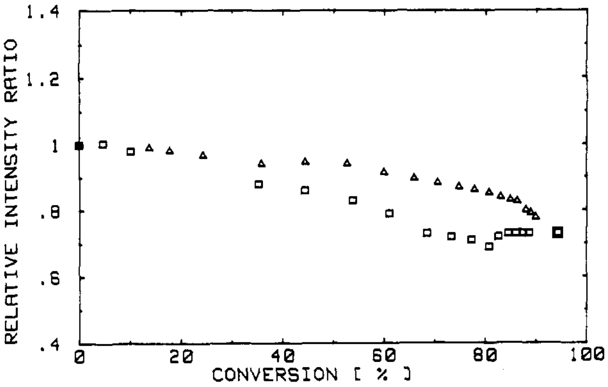

Figure 1. Relative intensity ratio of the 1000-cm^{-1} peak of styrene as a function of conversion: (□) 130 °C; (△) 160 °C.

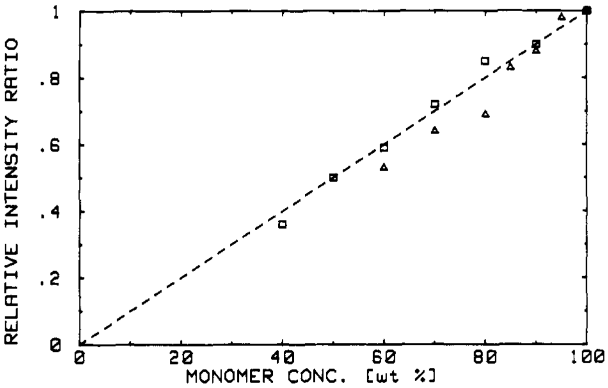

Figure 2. Relative intensity ratio of the carbon–carbon double bond as a function of monomer concentration: (□) styrene; (△) MMA.

heating, and mechanical frequency scanning are involved. In comparison to Figure 1, in Figure 2 we have plotted the intensity of the C=C bond stretch at 1631 cm^{-1} as a function of monomer concentration for a set of samples prepared by dissolving NBS standard polystyrene (706) in distilled styrene. We see that the peak area of the 1631-cm^{-1} band is linear with concentration. The message one gets from the previous results and Figures 1 and 2 is clear: if the spectrometer is mechanically stable and the sample does not become turbid or develop bubbles in the scattering volume, it is better to use the absolute peak areas. As a result we have used the peak area of the 1631-cm^{-1} band to measure conversion quantitatively. (Since in all of our measurements the 1000-cm^{-1} band was also measured simultaneously, we also used the normalization method to double-check our conversions.)

A total of four polymerization runs was made with styrene. Figure 3 shows the results of two runs, one with 0.5% AIBN (azobis(isobutyronitrile)) initiator at 80 °C and another at 140 °C without an initiator. The run with initiator was made in order to check whether we could observe the Trommsdorf effect at this low temperature. The conversion vs. time behavior of the sample containing initiator is significantly different from that of the uninitiated ones. During the polymerization process the rate of polymerization remains essentially constant, going from a high of 32%/h initially to a low 17%/h at 160 min and again increasing to 27%/h at 220 min. There is a small jump in conversion between 100 and 120 min, due to an accelerated rate of reaction.

The second set of data in Figure 3 was obtained by polymerizing the sample in an oil bath at 140 °C and taking it out and chilling before taking the spectra at regular intervals. In this way we also hoped to test the stability and reproducibility of the spectrometer. The low level of scatter in the data shows that our absolute peak area measurements were quantitatively reliable, even with this taking in/taking out procedure. The rate of polymerization behaves as expected: a faster rate initially, which decreases as the monomer is consumed.

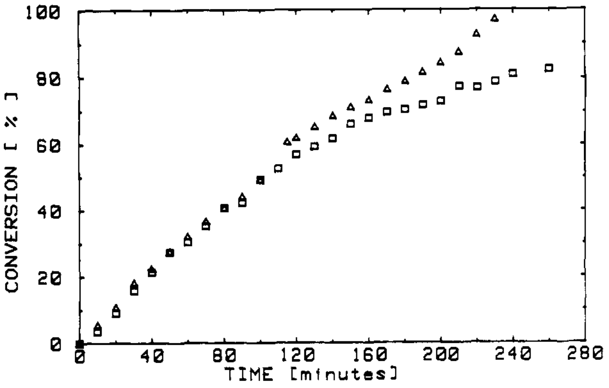

Figure 3. Conversion vs. time curves of styrene polymerization: (△) 80 °C, initiated with 0.5% AIBN; (□) 140 °C, uninitiated, heated in an oil bath.

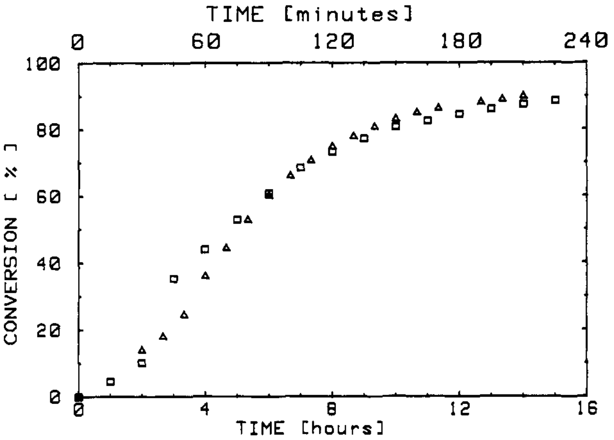

Figure 4. Conversion vs. time curves of styrene polymerization: (□) 130 °C (lower time scale); (△) 160 °C (upper time scale).

Figure 4 shows the results of two polymerization runs without an initiator. Note that the time scales are very different but the shapes superimpose quite well. In both cases the samples were polymerized inside the spectrometer. As a result, no mechanical disturbances were introduced from the beginning to the end of the experiment. In both sets of data we observe an increase in the rate of polymerization around 20–30% conversion. We did not see this increase in the data of Figure 3. The Trommsdorf effect (or gel effect) has been observed in thermal polymerization of styrene by Chu[6] at 65% conversion and by Alms[4] around 30% conversion, both at 90 °C. We are not sure why we did not observe a similar phenomenon with the 140 °C sample, unless the process was slowed down by the frequent chilling of the sample. The relative increase in rate is higher for the 130 °C polymerization, in agreement with what is known about the Trommsdorf effect in styrene polymerization.[8]

The initial rate of polymerization is 6%/h at 130 °C and 30%/h at 160 °C, yielding an activation energy of 19 kcal. These initial rates are in good agreement with both the classical measured rates[9] and the rates calculated by extrapolating Sears'[7] data of 0.5%/h at 70 °C and 2%/h at 100 °C. The activation energy is the same with those determined by Chu[6] and by classical methods.[9]

(b) Methyl Methacrylate Polymerization. As in the styrene polymerization case we first checked whether an internal calibration standard was needed or not. Figure

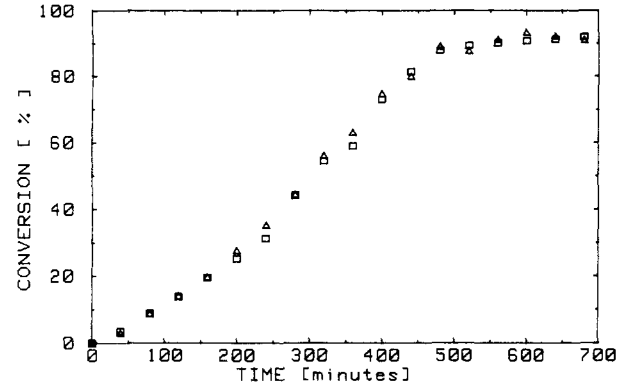

Figure 5. Conversion vs. time curves of MMA polymerization: (△) 1062-cm^{-1} polymer band; (□) 1643-cm^{-1} monomer band.

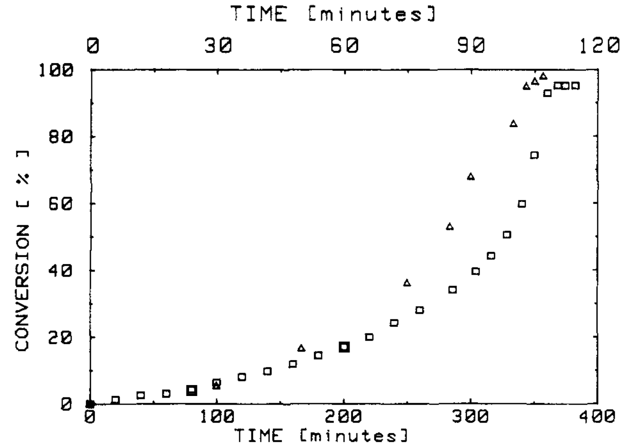

Figure 6. Conversion vs. time curves of MMA polymerization: (□) 100 °C (lower time scale); (△) 130 °C (upper time scale). Note that the rate of polymerization increases significantly around 50% conversion.

2 shows the Raman intensity of the 1631-cm^{-1} carbon–carbon double-bond symmetric stretch band as a function of monomer concentration. Due to difficulties associated with preparing uniform monomer–polymer mixtures, the calibration data could not be extended to lower monomer concentrations than 60%, but all indications are that the intensity changes linearly with the monomer concentration.

Figure 5 shows the results of an FTIR run at 75 °C. The conversion was determined two ways: by measuring the integrated area of the monomer C=C peak at 1643 cm^{-1} and the polymer peak at 1062 cm^{-1}. The rate of polymerization increases by a factor of 2–3 around 50% conversion but the increase is nowhere as sudden as that observed with the vacuum-sealed Raman samples, as will be shown later. Another run was done at 70 °C using 0.5% AIBN, which yielded a similar curve, the only exception being a more pronounced increase around 50% conversion.

Figure 6 shows the results of two polymerization runs in the Raman spectrometer. Both samples were in sealed cells and did not have any initiator. The initial rate of polymerization is 4.3%/h at 100 °C and 15%/h at 130 °C, yielding an activation energy of 9.6 kcal. These initial rates are significantly higher than the spontaneous polymerization rates observed for MMA and indicate the presence of peroxide impurities.[10] The Trommsdorf effect is much more visible in these samples. The rate increases significantly around 50% conversion for both samples. The increased rate is at least an order of magnitude greater than the initial rate, and ~50% of the remaining monomer is polymerized within 30 min at 100 °C. In relative terms the increase in rate is higher at the lower temperature as expected.[8]

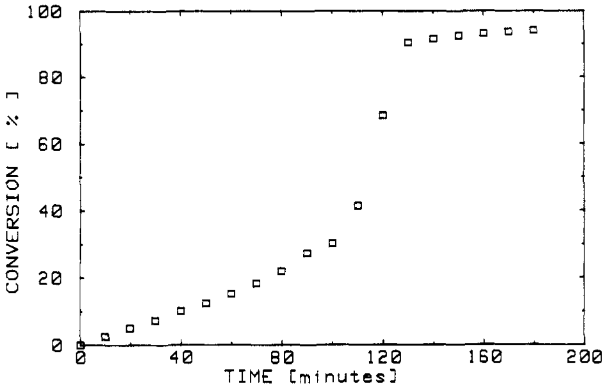

Figure 7. Conversion vs. time curves of MMA polymerization at 60 °C (initiated with 0.5 wt% of AIBN).

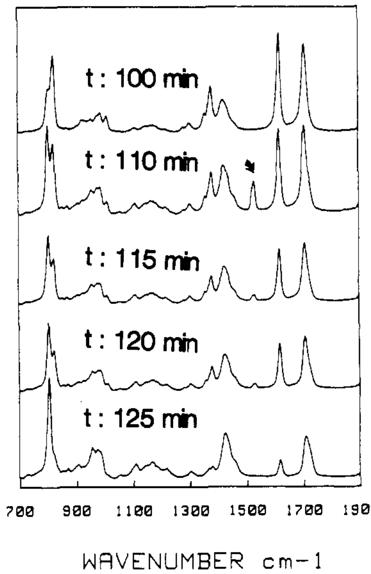

Figure 8. Several Raman spectra of the AIBN-initiated MMA system at 60 °C. Note that the 1545-cm^{-1} band is present only during the rapid polymerization period.

(c) Detection of a Reaction Intermediate. Perhaps the most interesting finding of this research was made when we decided to investigate AIBN-initiated bulk polymerization of MMA. Figure 7 shows the conversion as a function of time at 60 °C with a starting concentration of 0.5% AIBN. The rate of polymerization is linear with time at 18%/h until approximately 80 min (~25% conversion). When conversion reaches 35%, the gel effect starts (105 min total elapsed time), the polymerization rate jumps to 400%/h and the reaction goes essentially to completion withhin 20 min (125 min total elapsed time). Figure 8 shows a sequence of Raman spectra for this sample starting at t = 100 min. For the t = 110 min spectra, a new and quite strong peak at 1545 cm^{-1} is present. The intensity of this peak decreases with time and the peak is not detectable at t = 125 min. In order to make sure that this was not an artifact, we repeated the experiment and were able to observe its presence at precisely the same location, at the onset of the Trommsdorf effect. We have examined all of our spectra for the other polymerization runs, initiated and uninitiated with styrene and uninitiated MMA runs, and have not been able to detect the presence of this peak. This peak is also not visible in the initiated MMA IR spectra. In order to make sure that this peak was due to a reaction intermediate and not due to AIBN itself, spectra of dissolved AIBN in acetone (to stimulate the polar MMA environment) was investigated at the same temperature with negative results.

On the basis of these preliminary results, we conclude that the peak is due to a free radical intermediate formed by the addition of AIBN to MMA or by AIBN in MMA. This free radical is probably stabilized through conjugation with either the cyano group or the ester group. The fact that we were able to obtain a good signal from a reaction intermediate which presumably is very low in concentration and relatively short-lived suggests that there must be a significant enhancement of the Raman band by resonance. Since our excitation wavelength was 488.0 nm, a conjugated system is needed. We plan to check whether the signal is due to resonance Raman scattering or not in the near future.

IV. Conclusions

We have successfully demonstrated the use of Raman and FTIR spectroscopy for monitoring polymerization of styrene and MMA in real time. Contrary to the previously recommended procedure, monitoring only the integrated peak area of the double-bond peak at 1631 cm^{-1} for Raman and 1643 cm^{-1} for IR introduces less total error compared to using an internal reference band. The activation energies and the initial rates of polymerization determined from spectroscopic data compare very favorably with the classical data for styrene polymerization.

We see a lower rate of polymerization in our IR cell than the Raman cell. This can be due to the fact that the IR cell has a high surface-to-volume ratio compared to the Raman cell. Another possibility is the presence of oxygen and a lot of metallic surface in the IR cell. We observe some indications of the Trommsdorf effect with thermal polymerization of styrene but it is much more readily observable for MMA polymerization.

This investigation also shows the value of simultaneous detection of a wide frequency range of the Raman spectrum. As a result of the fact that we detected all the signal in a 1300-cm^{-1} range, we were able to observe the presence of a reactive intermediate, probably a stabilized free radical, when the polymerization rate increases in the initiated MMA system. We are planning on continuing our research in this area in order to find out more about the reactive intermediates.

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Registry No. Styrene, 100-42-5; methyl methacrylate, 80-62-6.

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Hydrodynamic Thickness of Adsorbed Polymer Layers

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ABSTRACT: Hydrodynamic thicknesses of adsorbed polymer layers have been calculated on the basis of a porous layer model using segment density profiles calculated with the Scheutjens–Fleer adsorption theory. Comparisons of the molecular weight and adsorbed amount dependence of the hydrodynamic thickness are made with experimental data obtained by photon correlation spectroscopy on a system of polystyrene latex particles dispersed in aqueous poly(ethylene oxide) solutions. It is confirmed that tails play a very important role in the screening of the adsorbed layer from the flow field.

Introduction

An early study of Öhrn[1] was the first to appreciate the considerable effect of an adsorbed polymer on liquid flow through a capillary. More recently, this effect has been exploited by a number of research groups in order to characterize adsorbed layers by means of a "hydrodynamic" thickness. The experimental techniques used are in most cases based on the reduction of flux of solvent when a polymer is adsorbed on the wall of a suitable flow channel. Various materials have been used, for example, sintered glass disks,[2] porous membranes, single glass capillaries,[3] or capillary arrays. An alternative approach is to measure the increase in radius of a colloidal particle upon adsorption by means of its sedimentation[4] or diffusion[4,5] coefficient.

Because of difficulties in the interpretation of the hydrodynamic thickness, the interpretation of experimental data has been purely qualitative. However, in a recent paper Varoqui and Degardin[6] have given an analytical solution of an appropiate hydrodynamic equation for the case of a capillary with an adsorbed layer. Their approach is instructive as it gives an explanation for the experimental observation that the hydrodynamic thickness is often much larger than the layer thickness determined