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Complexes in polymers IV. FTIR microscopic characterization of thin organic polymer films containing embedded transition-metal carbonyl complexes

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Thin films of polystyrene (PS), poly(methyl methacrylate) (PMMA) and polystyrene–polyacrylonitrile copolymer (PS–AN), containing various embedded transition-metal complexes, have been studied by FTIR microscopy. The spatial distributions of the transition-metal carbonyl complexes throughout the thin organic polymer films have been determined by a two-dimensional IR mapping procedure. The spectral variations observed in the distribution of the metal carbonyls throughout the different polymer films are discussed. The IR data show that the technique used to prepare the organometallic-embedded thin films (viz. freeze-drying of solutions followed by hot mechanical pressing of the residues) does in general lead to homogeneous films which may eventually find industrial application, e.g. as membrane sensors for small molecules.

Keywords: Organometallic compounds, polymer, FTIR spectroscopy, microscopy, two-dimensional mapping

INTRODUCTION

In a series of recent papers, we have described the production and certain physicochemical properties (e.g. photochemistry, electrochemistry and polarization behavior) of thin films of polystyrene (PS), poly(methyl methacrylate) (PMMA), polystyrene–polyacrylonitrile (PS–AN), and polythiophene (PTP) containing embedded transition-metal carbonyl complexes.[1-6] These polymer films may eventually find application as membrane sensors for small molecules such as CO, SO_2, Cl_2, etc., or in the pressure-swing recovery of CO from flue gas. We have shown that FTIR spectroscopy in the CO stretching region (2200–1800 cm^{-1}) is an extremely useful way of characterizing the films. Although it was thought that the transition-metal carbonyls were distributed homogeneously throughout the films, this was never established conclusively. Consequently, we decided that it would be worthwhile investigating this problem by FTIR microscopy and we report our results in this paper.

EXPERIMENTAL

The metal carbonyl complexes embedded in the polymer films, $Cr(CO)_6$, $W(CO)_6$, $(\eta\text{-}C_6H_6)Cr(CO)_3$, $CpMn(CO)_3$ ($Cp = \eta\text{-}C_5H_5$), $[CpMo(CO)_3]_2$, $Mn_2(CO)_{10}$, $[CpFe(CO)_2]_2$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, were purchased from Strem Chemical Co. The polymers, PS, PMMA and PS–AN (75:25 wt%), were supplied by Polysciences. Since the preparation of the metal carbonyl-embedded polymer films has already been described in detail elsewhere,[2] only a brief summary will be given here. The metal carbonyl complex (~0.05 g) and polymer (1 g) were dissolved in benzene under a nitrogen atmosphere. The solution was stirred vigorously and frozen, and then the solvent was quickly removed by freeze-drying. The resulting fluffy residue was pressed at 3000 psi (2.1×10^4 kPa) at 120 °C for 30 min to yield the required thin film.

The IR spectra of the thin films were recorded at ambient temperature at 1 cm^{-1} resolution on a Bruker model IFS-48 spectrometer fitted with an A-590 IR microscope equipped with a liquid nitrogen-cooled mercury–cadmium telluride detector. In a typical IR microscopy measurement, the thin film, supported on a potassium bromide disc, was located in the IR beam of the microscope (operating in the transmission mode) under the 36× objective (Ealing) with the post-objective aperture set to 0.3 mm. Under these

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conditions, a spot of ~8 μm cross-section could be examined. In those cases where intensity considerations, either because of lack of signal or signal overload, did not permit the collection of useful spectral data, the spectra were recorded against an air background by suspending the films directly in the path of the IR beam. Whenever possible, the minimum practical aperture and maximum practical magnification were used. The exceptions were for $(\eta\text{-}C_6H_6)Cr(CO)_3$/PMMA and $[CpFe(CO)_2]_2$/PMMA (36×, 0.3 mm aperture), $W(CO)_6$/PS–AN (for concentrations >20%; 15×, 3 mm aperture, effectively 200 μm), $Ru_3(CO)_{12}$ (36×, 3.75 mm aperture, effectively 104 μm) and $Mn_2(CO)_{10}$ (36×, no aperture, actually 500 μm). The spatial distributions were assessed by comparing the integrated IR intensities of the CO stretching bands in the 2200–1700 cm^{-1} region along perpendicularly oriented transects which intersected near the centres of gravity of the film fragments. In general, the IR measurements were taken at 0.5 mm intervals for a distance of 2.0 mm in each direction from the central point.

RESULTS AND DISCUSSION

The IR spectra of the thin films at any given location provided information about both the polymer films and the metal carbonyl complexes embedded in them. The CO stretching regions of these organometallic materials were known to be comparatively free from any interference from the polymer vibrations.[1,2] In the case of PS and PS–AN, there was a series of broad overtone bands appearing in the ν(CO) region, but these bands could be easily subtracted out and were apparently unperturbed by the presence of low concentrations (~5%) of the metal carbonyl dopants. The strong PS band at 1601.4 cm^{-1} served as a convenient reference for monitoring the properties of this polymer. The thin films used in the present work had been stored in sealed tubes under nitrogen in a refrigerator for some time prior to spectroscopic examination. The age of the films was not a problem because we had shown earlier that films stored in this manner were stable for several years.[1]

For the most part, the thin films were transparent to both visible and IR radiation, and their *colour* depended on the type and concentration of the metal carbonyl substrate present. Some exceptions were the high-concentration $W(CO)_6$/PS–AN films, which were white and translucent to visible and nearly opaque to IR radiation, and the $Ru_3(CO)_{12}$ film, which was dark red, highly reflecting and virtually opaque to both visible and IR radiation.

Microscopically, the films exhibited a series of parallel features across their surfaces, presumably due to the pressing process. Most of the films contained minute crystals, about 1–5 μm in cross-section, distributed evenly across the film surfaces. Some of the films were marred by larger (20–30 μm) clumps of crystals. All the films containing $W(CO)_6$, and the PS–AN and PMMA films containing $Os_3(CO)_{12}$, had grainy textures, which proved difficult to render in focus under the microscope. On the other hand, the $(\eta\text{-}C_6H_6)Cr(CO)_3$/PMMA films were visually extremely uniform and contained no observable blemishes other than the parallel surface features. None of these visually detectable features correlated in any systematic manner with variations in the IR spectra.

Polymer vibrations

The integrated intensities of the PS vibrations (with reference to the 1601.4 cm^{-1} fundamental and the overtone bands in the 2000–1600 cm^{-1} region), remained essentially constant (<1% variation) across the observed spatial distributions within each sample. A few of the films did exhibit features of greater magnitude, particularly close to the edges of the film fragments. Variations in the IR cross-section could be attributable to changes in either the density or, more probably, the thickness of the polymer films.

In those cases where the intensities of the polymer bands did show variation, there were increases in intensity (and presemably also in the film thickness) towards the edges of the transects, with the only exception being a very small fragment of the $CpMn(CO)_3$/PS–AN film for which thinning occurred towards the edge of the transect (and also of the fragment itself).

The $W(CO)_6$/PS films proved to be somewhat exceptional, since a visually large agglomeration of crystals corresponded to a thickening of the film. This may well have been coincidental. Other unusual cases were the $Mn_2(CO)_{10}$/*PS and the* UV-irradiated $CpMn(CO)_3$/PS–AN films, both of which were very thin, colourless and had pitted segments. The modulations in the IR crosssections in these films were continuous and quite extensive, indicating poor film formation. These results suggest that the organometallic complexes in question interfere strongly with film growth.

While the spectral profiles of the polymers within a film remained relatively constant, the differences in IR cross-section between different films of the same polymer matrix were sometimes quite significant, particularly for the PS films, where the IR intensities varied by a factor of four on going from the thinnest to the thickest films. On the other hand, the IR intensities of the polymer vibrations in the metal carbonyl/PS–AN films were always lower than those for pure polymer films of approximately the same thickness, which had been produced by the same pressing technique. The variation between individual complex-doped films (0.3–0.6 times that of the non-organometallic-embedded films) was less than that between pure PS films.

The PMMA films did not exhibit any peaks particularly suitable for determining the polymer uniformity. The only useful peak close enough to the ν(CO) region was a very strong band centred at 1750–1720 cm^{-1} but this peak displayed a significant noise level at the peak maximum. Nevertheless, several less intense peaks far from the region of interest suggested that the PMMA films were at least as uniform as those of PS and PS–AN.

Whenever the films did exhibit IR variations of the type described above, the measured intensities of the ν(CO) peaks were normalized so that a constant polymer cross-section corresponding to that of the most uniform section of the observed film transect was obtained.

ν(CO) vibrations

Since the molar absorptivities of the IR-active CO stretching modes were expected to vary greatly over the range of complexes being investigated, we felt that there was no point in attempting to compare the absolute integrated intensities of individual peaks. Moreover, some of the complexes have several ν(CO) peaks, not all of which are clearly resolved and, in these cases, the integrated intensities were summed over all the ν(CO) peaks. The polymer backgrounds were spectrally subtracted prior to integration using a fully resolved polymer peak near to the ν(CO) peaks as reference. The spectral features associated with the organometallic complexes have been discussed in detail previously,[1–4] and no significant differences were observed in the present spectra.

Table 1 presents the range, expressed as the fraction of the mean of the integrated intensities of the ν(CO) bands, and the variance (standard deviation as a fraction of the mean) for each of the films examined. Two representative spectra showing the types of variation are illustrated in Fig. 1. While in many ways the embedded thin films resemble solutions of the organometallics in organic solvents,[1–4] they do not allow free diffusion of the metal carbonyl species within the bulk material. Thus, any concentration gradients formed during processing are quite likely to be observed upon moving from point to point across the film surfaces. The variances were generally between 5 and 20%, while the ranges were from 10 to 50%. Any exceptions to these values also exhibited other anomalous behaviour. For those films containing metal carbonyls with two or more resolved IR-active ν(CO) bands, the variances for the different bands agree to within a few per cent. Remarkably, different film fragments of the same composition show very similar values of variance and range (within 1–2%). The PMMA films generally have consistently lower variances than do the other films containing the same organometallic substrate. On the other hand, high variances were observed for the PS films. These results are consistent with earlier observations[2,3] that the PMMA films are the most stable and that the PS–AN and PMMA films stabilize the metal carbonyl substrates. The PMMA films are much less permeable than are the others. Our results also suggest that a PMMA matrix may resist the formation of concentration gradients during processing better than the others.

By using the small aperture on the microscope, 'snapshots' of the concentration profiles across the film centres could be obtained. The mapping technique afforded some information on the small-scale variations as a function of position, and it gave an indication of variations of greater than 1 mm in magnitude. The polymer films did exhibit a systematic variation on this scale, with most of the films displaying features of 1–4 mm cross-section. Some of the films, notably $Ru_3(CO)_{12}$/PS, exhibited large features (>8 mm cross-section). Figure 2 shows typical spatial distributions across two of the films. These films show random, but gradual, variations on the millimetre scale. Considering that the mapping procedure detects small spots separated by around 50 times their diameters, the variations must be

Table 1 Percentage variances and ranges for the ν(CO) bands of transition-metal carbonyl embedded polymer films investigated in this work.

Compound	Band[a]	Polymer	Variance (%)	Range (%)
$Cr(CO)_6$	t_{1u}	PS	11	42
$(C_6H_6)Cr(CO)_3$	a_1	PS	19	89
	e		28	138
$(C_6H_6)Cr(CO)_3$	a_1	PS–AN	15	57
	e		20	68
$(C_6H_6)Cr(CO)_3$	a_1	PMMA	3	10
	e		3	11
$[CpMo(CO)_3]_2$	II	PS	7	23
	III		7	26
$[CpMo(CO)_3]_2$	I	PS–AN	6	22
	II		6	31
	III		6	22
$[CpMo(CO)_3]_2$	I	PMMA	16	64
	II		5	21
	III		11	44
$W(CO)_6$	t_{1u}	PS	26	92
$W(CO)_6$ (21%)	t_{1u}	PS–AN	8	30
$W(CO)_6$ (31%)	t_{1u}		8	32
$W(CO)_6$ (40%)	t_{1u}		6	24
$Mn_2(CO)_{10}$	b_2	PS	77	190
	e_1		77	190
$Mn_2(CO)_{10}$	$b_2 + e_1$	PS–AN	38	133
$Mn_2(CO)_{10}$	b_2	PMMA	9	33
	e_1		8	30
	b_2		13	41
$CpMn(CO)_3$	a_1	PS	12	35
	e		11	32
$CpMn(CO)_3$	a_1	PS–AN	11	40
	e		6	25
$CpMn(CO)_2PS–AN$	a′	PS–AN	22	81
	a″		22	81
$[CpFe(CO)_2]_2$	a_1 (*cis*)	PS	17	52
	b_u (*trans*)		18	57
	a_u, b_1 (br)		18	57
$[CpFe(CO)_2]_2$	a_1 (*cis*)	PS–AN	16	58
	b_u (*trans*)		20	79
	a_u, b_1 (br)		17	60
$[CpFe(CO)_2]_2$	a_1 (*cis*)	PMMA	8	36
	b_u (*trans*)		7	28
	a_u, b_1 (br)	8	28	
$Ru_3(CO)_{12}$	Total[b]	PS	19	73
$Os_3(CO)_{12}$	Total[b]	PS	15	67
$Os_3(CO)_{12}$	Total[b]	PS–AN	6	32
$Os_3(CO)_{12}$	Total[b]	PMMA	9	37

[a] The band positions can be found in Refs 1–5; br = broad. [b] Integration over the complete ν(CO) range.

remarkably uniform in order to be so clearly discernible.

Two of the films (η-C_6H_6)$Cr(CO)_3$/PS–AN and $Mn_2(CO)_{10}$/PS–AN, showed concentration ridge features several millimetres long and of less than 1 mm cross-section. Detection of these very narrow features was purely fortuitous using the present sampling technique. While a complete mapping of the surface would always detect such features, this procedure would be prohibitively time-consuming. However, these spectral features are no more than 50–100% greater in intensity than the peaks of the polymer film matrix. Despite these identifiable concentration features, the overall variance in the (η-C_6H_6)$Cr(CO)_3$/PS–AN film was well within

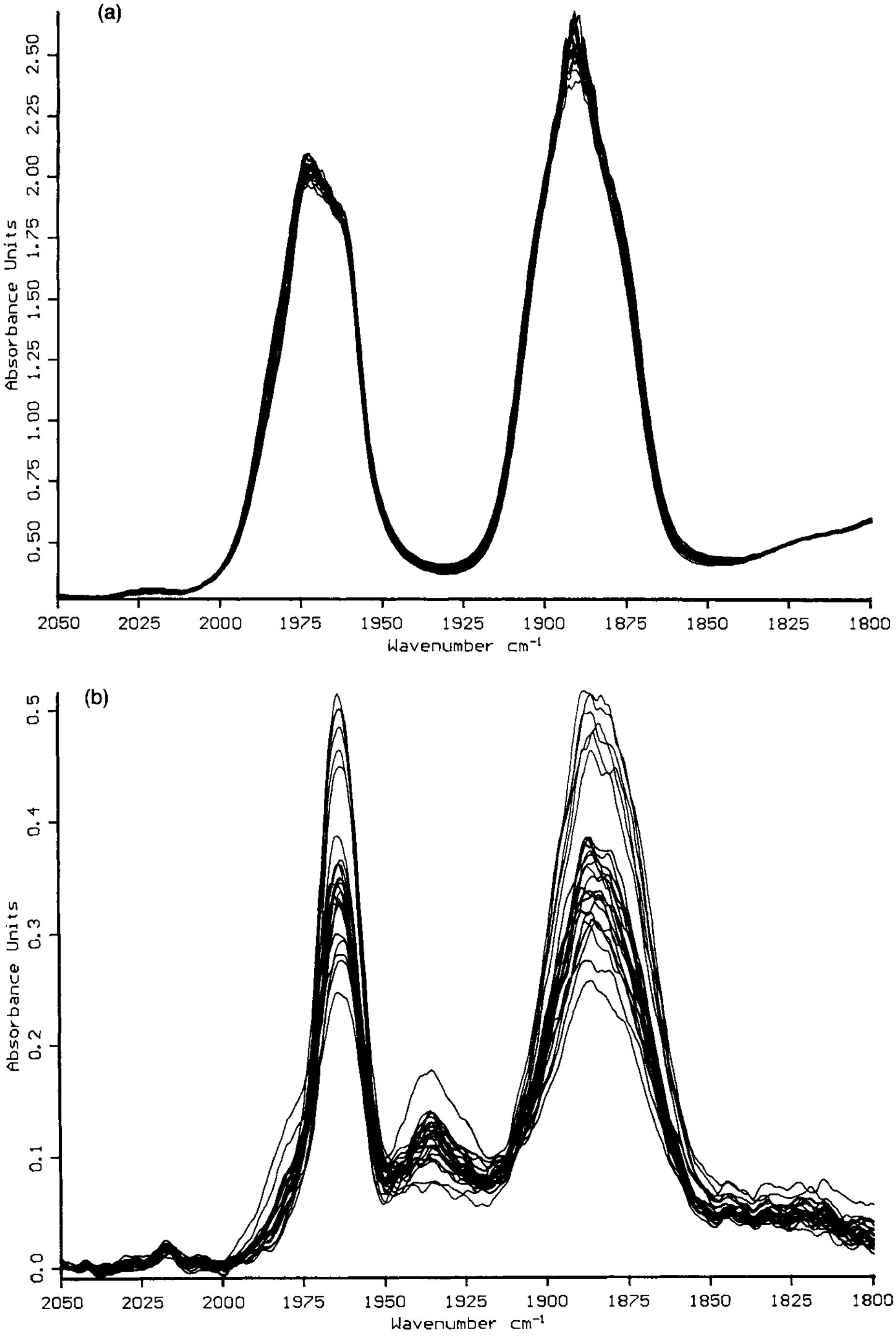

Figure 1 (a) Overlay of the FTIR (microscopy) spectra of the (η-C_6H_6)$Cr(CO)_3$/PMMA film throughout the spatial region investigated; (b) as in (a), but in PS–AN film.

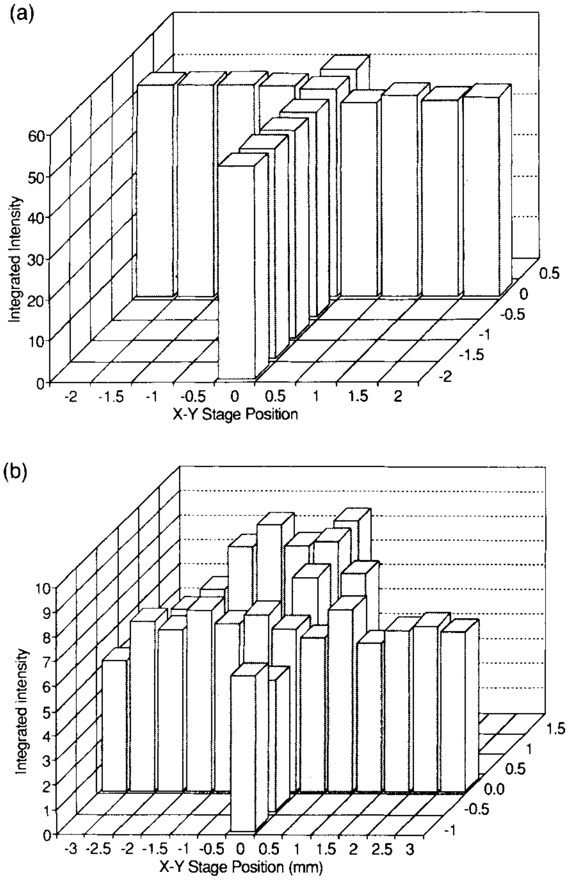

Figure 2 (a) Map of the intensity of the a_1 $\nu(CO)$ peak of $(\eta\text{-}C_6H_6)Cr(CO)_3$/PMMA film plotted against distance (in mm) from the centre of the transects (see text); (b) as in (a), but in PS–AN film.

the normal range. The reason for the higher variance in the $Mn_2(CO)_{10}$/PS–AN film is not clear.

Two further examples, $Mn_2(CO)_{10}$/PS and $CpMn(CO)_3$/PS–AN, stand out for their thinness, clearly observable to the naked eye, and the great variations in the polymer cross-section. Even after normalization to account for the polymer thickness profile, the $Mn_2(CO)_{10}$/PS film showed large, random concentration fluctuations which seemed to have no relation to the variation in thickness. The overall concentration of the organometallic complex in this particular film was very low, with a CO stretching vibration intensity an order of magnitude lower than in other $Mn_2(CO)_{10}$-containing films. It is unlikely that this effect is entirely due to molar absorptivity differences. In order to obtain a sufficiently intense IR signal, this particular sample had to be examined at low magnification (15×) without any aperture reduction and at 10× gain amplification, while collecting ten times the number of scans used for the other films.

Some measurement difficulties also occurred for films containing very high concentrations of certain metal carbonyls. These difficulties arose because almost all of the incident IR radiation was absorbed, leaving only a small output to be measured. To combat this problem, a high throughput was allowed, producing a measurable absolute level of transmitted radiation. This behaviour was especially important for the high-concentration $W(CO)_6$/PS–AN films and for the ruthenium carbonyl $[Ru_3(CO)_{12}]$ film. In these cases, only a single, very broad, intense band, some 200 cm^{-1} wide with a high noise level at the top of the peak, was observed. The data for the highly doped films ($W(CO)_6$; 31% and 40% in PS–AN) are probably less reliable than for the other films. This is evident from a comparison of the relative intensities of the $\nu(CO)$ bands in the 21%, 31% and 40% films. While the 21% film is consistent with a concentration 20 times that of the standard film, the 31 and 40% films appear to be only a few per cent more concentrated.

One of the organometallic solutes, $[CpFe(CO)_2]_2$, exists in solution[7] and in polymer films[3] as *cis* and *trans* isomers. Although the earlier observation of the dependence of the *cis*/*trans* ratio on the type of polymer was substantiated in the present work, as expected, there was no detectable variation in the isomer distribution across the film transects.

CONCLUSIONS

Microscopic observation of the FTIR spectra at specific small-diameter locations across metal carbonyl-embedded polymer films is a useful technique for measuring the uniformity of such films. Using this method, it has been established that the available organometallic films were generally uniform in both concentration and thickness. Any variations in concentration were smooth on the scale of 3–4 mm in space across the films. The most common gradient was a slight thickening of the films towards the edges of the fragments, most probably resulting from the pressing procedure employed for small pieces. Several films exhibited remarkable uniformity while others displayed very appreciable variability in either concentration or thickness. In particular, some of the films showed incompatibility with the method of preparation. As found earlier for certain oxidation and photochemical reactions,[3] PMMA is a more ideal support than is either PS or PS–AN.

Polymer films containing embedded organometallic compounds are of interest in relation to supported reactions of the metal carbonyl substrates. Hence, the uniformity of the films is of importance since the efficiency of such reactions is dependent upon the cross-section of the reactive site. The diffusion of reagents into the film and to reaction centres at the metal are dependent on film thickness and substrate concentration. For radiation-absorbing applications[8,9] the uniformity is crucial to the protective or photochemical efficiency. It is clear that care must be taken in the selection of substrate and medium. Although film compositions are generally uniform, careful, informed selection can afford especial uniformity. Similarly, poor, uninformed selection can produce mixtures incompatible with the film production process. Polymers such as PS–AN and PMMA which offer polar functionalities are definitely superior in uniformity to the pure hydrocarbon species (PS). $Mn_2(CO)_{10}$ is a particularly difficult substrate with which to work. High concentrations of a metal carbonyl complex can interfere with spectroscopic applications such as calibration standards.[1] Finally, the present work suggests that caution must be exercised with post-fabrication reactions involving embedded organometallic complexes because of the possibility of concentration gradients being formed.

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