

## Cryochemical Synthesis of Mn-Containing Poly(*p*-Xylylene)

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A Mn-containing polymer was produced by solid-state photopolymerization of a cocondensated mixture of *p*-xylylene with Mn at 80 K. It was shown that during simultaneous deposition *p*-xylylene and Mn formed both  $\sigma$ - and  $\pi$ -complexes. Irradiation of the system by UV light resulted in polymerization of *p*-xylylene with the destruction of the unstable  $\pi$ -complexes, while the  $\sigma$ -bonded compounds were incorporated into the polymer chains. Complexes of Mn with benzyl-type radicals of the polymerized system were also observed. Prolonged storage of the polymerized material at ambient temperature under vacuum led to the gradual decomposition of the organomanganese compounds and complexes.

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**KEY WORDS:** Manganese-*p*-xylylene complexes; metal polymer; cryochemical synthesis.

### INTRODUCTION

Metal-containing polymer systems are of considerable interest for both fundamental science and various chemical and technical uses [1, 2]. Among these systems are polymers with organometallic units in polymer chains, complexes of metals with polymers, metal clusters, and nanocrystals in polymer matrices [1]. Usually three methods are used for metal-polymer synthesis: treatment of polymers with metal vapors [1], reduction of metal salts in polymer systems [3–6], and polymerization of a monomer in the presence of metals [7–13]. The latter method can give

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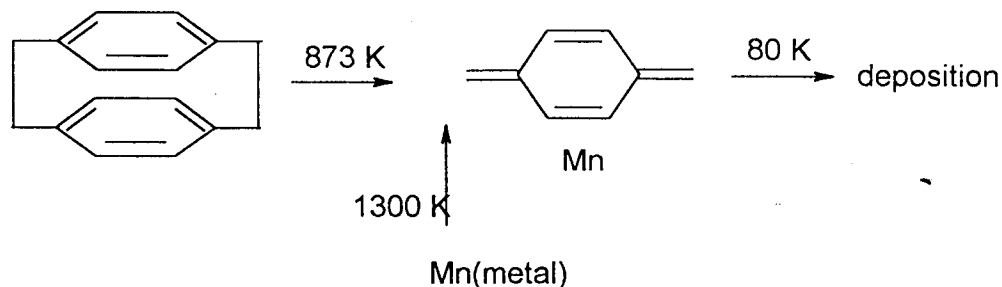
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polymer chains with organometallic units. There are various polymerization reactions available to produce a metal-polymer system: plasma polymerization in the presence of metal vapors [8–10], polymerization during low-temperature codeposition of monomers and metals [7, 11], and polymerization of liquid monomer-metal mixtures [12, 13].

Our work is based on low-temperature, solid-state polymerization reactions [14–16]. We use *p*-xylylenes as monomers. These are characterized by a high reactivity in the solid state [17] and polymerize quantitatively under uv irradiation at liquid nitrogen temperature [16]. Recently, it has been shown that cocondensation of *p*-xylylene (PX) and magnesium (Mg) at 80 K followed by polymerization of the cocondensate produces poly-*p*-xylylene [poly(PX)] with organomagnesium units in the polymer chains [18, 19]. The present paper deals with the preparation and polymerization of a low-temperature cocondensed system of PX with manganese (Mn). The system was characterized by ir and uv-visible spectroscopies. It was established that the original cocondensates contain  $\sigma$ -bonded organomanganese compounds along with PX-Mn  $\pi$ -complexes. Photoinitiated polymerization at 80 K causes destruction of the  $\pi$ -complexes and rearrangement of the organomanganese compounds, with incorporation of the latter into the polymer chains. Complexes of Mn with benzyl-type radicals have also been observed. The complexes and compounds of Mn formed by low-temperature cocondensation followed by polymerization turned out to be metastable and were gradually destroyed after heating the system to ambient temperature.

## EXPERIMENTAL

PX was produced by gas-phase pyrolysis of *p*-cyclophane at 873 K [20]. PX vapors were deposited onto a substrate of quartz or KRS-5 simultaneously with condensation of Mn vapors produced by sublimation of metallic Mn at 1250–1300 K in a special optical cryostat at 80 K (Scheme I). Construction of the cryostat and details of the deposition are



Scheme I

described elsewhere [16, 18]. The PX–Mn mixtures that were obtained were polymerized at 80 K under uv irradiation from a high-pressure mercury lamp. The thickness of the films was between 1 and 2  $\mu\text{m}$  [18].

The uv–visible spectra of the initial and polymerized films were measured using a Shimadzu 365 spectrometer. The ir spectra were recorded with a Perkin–Elmer 580 spectrophotometer.

The molar fraction of Mn ( $X_{\text{Mn}}$ ) was calculated as  $X_{\text{Mn}} = M_{\text{Mn}} / (M_{\text{Mn}} + M_{\text{PX}})$ , where  $M_{\text{Mn}}$  and  $M_{\text{PX}}$  are the amounts of Mn atoms and PX molecules, respectively.  $M_{\text{Mn}}$  was measured by atom absorption spectroscopy. Polymerized films of known weight were burned in  $\text{O}_2$  and the residual solid material was treated with a predetermined quantity of aqueous HCl to dissolve the manganese oxide. The  $\text{Mn}^{+2}$  absorbance in vapors of the solution at a wavelength of 279.5 nm was registered with a Perkin–Elmer 503 spectrometer and correlated with a standard. According to the measurements, the Mn concentrations in different samples were between 10 and 30%.

## RESULTS AND DISCUSSION

The ir spectra of the PX–Mn films with different Mn contents (10 and 30%) before and after uv irradiation are presented in Figs. 1a and 2a. The systems produced by cocondensation of PX with Mn at 80 K show the absorption bands of the quinonoid PX [21] at 470, 870, and 1590  $\text{cm}^{-1}$ . The higher frequency band is clearly seen in the spectrum of the film with the lower Mn content (Fig. 1a), while the spectrum of the PX–Mn condensate with the higher Mn concentration the same band is exhibited as a shoulder (Fig. 2a). Thus, not all of the *p*-xylylene molecules were bound to Mn even at a 30% concentration. The absence of the absorption bands of poly(PX) [22] in the spectra shows that simultaneous cocondensation of PX with the transition metal onto a substrate at 80 K does not lead to the polymerization of PX. In addition to the bands of free PX, there are some new bands at 1570, 1480, 1210, 1160, 950, and 740  $\text{cm}^{-1}$  in the ir spectra of the original Mn–PX system. These bands are not observed in the spectrum of pure PX. Since the relative intensities of the new bands increase with increasing Mn concentration (compare Figs. 1a and 2a), we conclude that they belong to the Mn–PX compounds that are obtained during the cocondensation process.

It is noteworthy that the bands at 1480, 1210, 950, and 740  $\text{cm}^{-1}$  coincide with those in the ir spectrum of the PX–Mg condensate that were assigned to vibrations of an organomagnesium compound with the following unit structure.

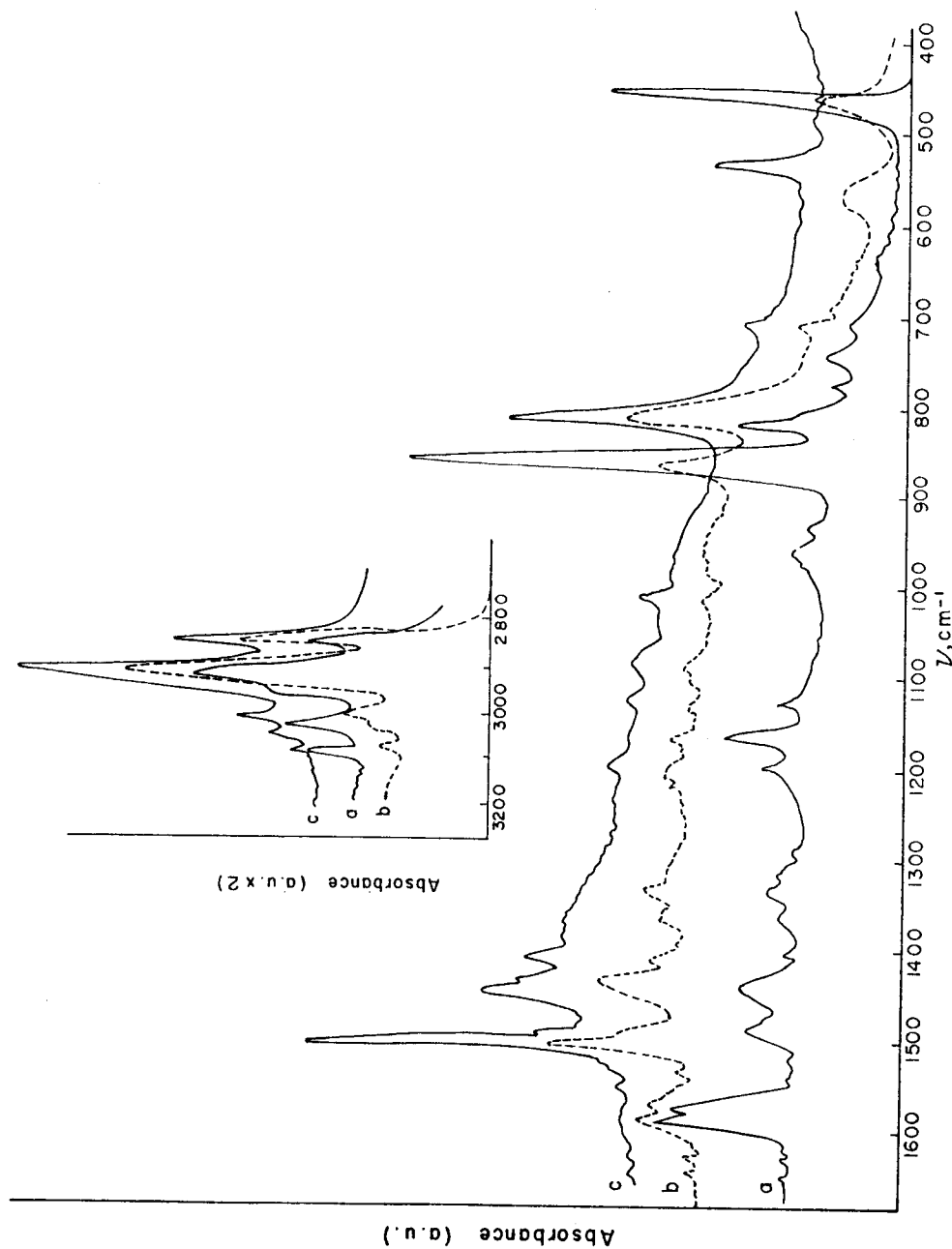


Fig. 1. The ir spectra of the PX-Mn films with a Mn concentration of about 10 mol%. (a) Original cocondensate at 80 K; (b) after uv irradiation at 80 K; (c) after annealing to room temperature.

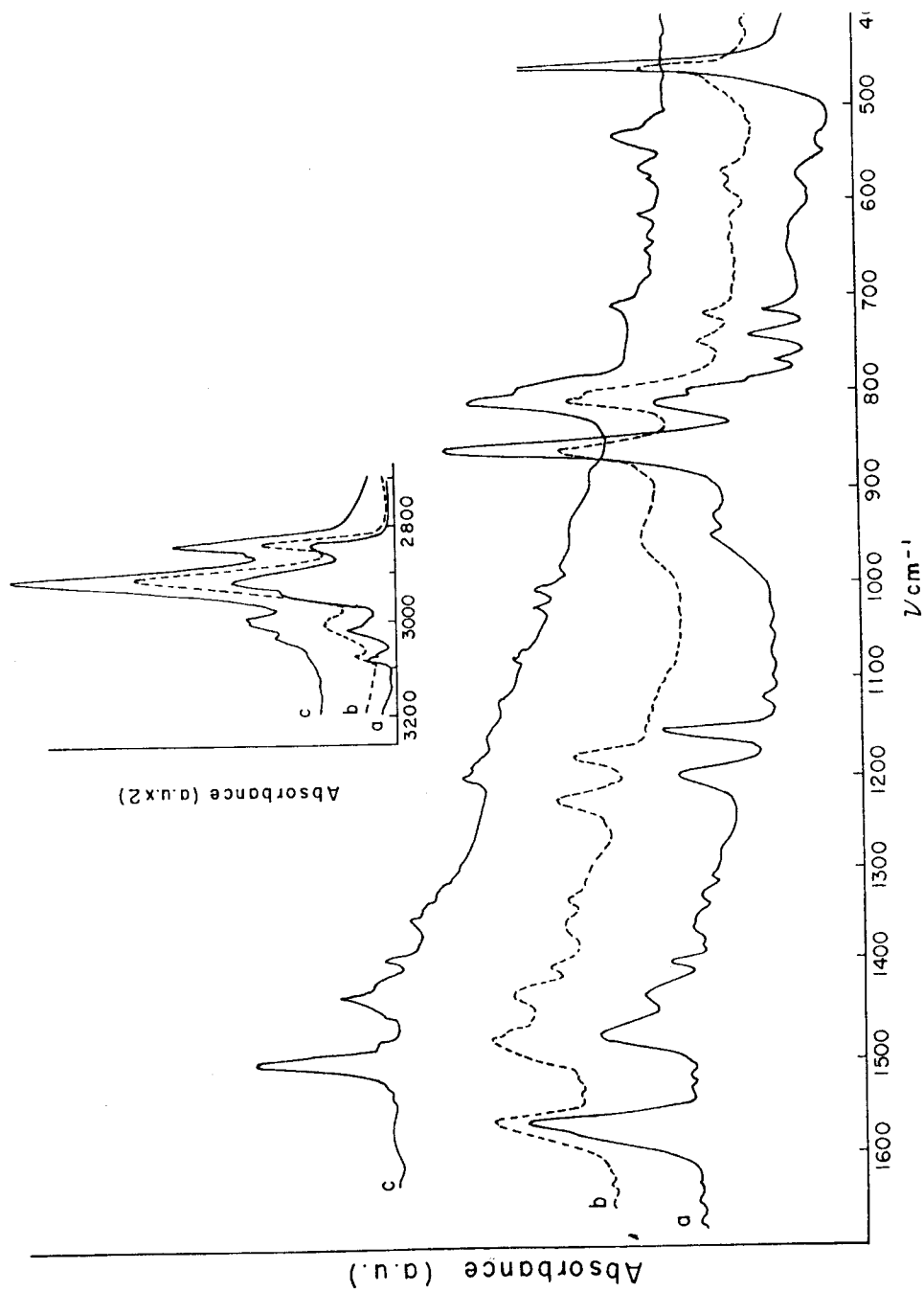
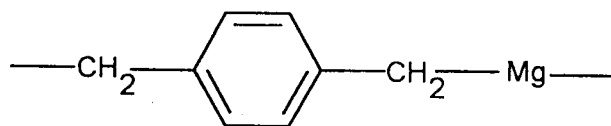
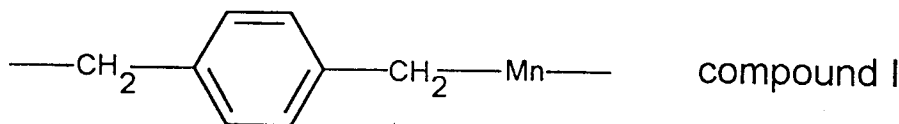


Fig. 2. The ir spectra of the PX-Mn films with a Mn concentration of about 30 mol%. (a) Original condensate at 80 K; (b) after uv irradiation at 80 K; (c) after annealing to room temperature.



By analogy, we conclude that the same bands arise from a similar  $\sigma$ -bonded complex of PX with Mn (compound I), and, the assignment of ir bands given elsewhere can be applied here.



In particular, the band at  $1480\text{ cm}^{-1}$  is most likely the C–C stretching vibrations in the benzene rings. This band is shifted to a lower-frequency region relative to the analogous band in the spectrum of poly(PX) at  $1510\text{ cm}^{-1}$ . The shift may be interpreted in terms of an electron transfer from Mn to the benzene ring. The band at  $1210\text{ cm}^{-1}$  is related to the stretching vibrations of the strongly polarized bonds in the Mn–C bond and the benzene ring [18]. The same vibrations of CH<sub>2</sub>–benzene ring bonds in pure poly(PX) give only a very weak absorption band at  $1200\text{ cm}^{-1}$ .

There are also bands attributed to the  $sp^3$ -hybridized CH<sub>2</sub> groups at  $2920$  and  $2850\text{ cm}^{-1}$  in the spectrum of the original cocondensate. The relative intensities of these bands depend on the Mn content in the system (Figs. 1a and 2a). These bands can be assigned to CH<sub>2</sub> groups of PX  $\sigma$ -bonded with Mn since poly(PX) is not formed during the cocondensation.

The absorption bands near  $950\text{ cm}^{-1}$  may be attributed to the highest-frequency out-of-plane C–H vibration mode of the benzene ring [23, 24]. This mode leads to an appreciable distortion of the  $\pi$ -electron system of the benzene ring that results in a change of the electron transfer from Mn to the benzene ring. Such an effect may be responsible for the much higher intensity of these bands in the Mn–PX system compared with those of pure poly(PX). The absorption band at  $740\text{ cm}^{-1}$  may be assigned to the rocking vibrations of the negatively charged CH<sub>2</sub> groups in the MnCH<sub>2</sub> unit [25]. Stretching vibrations of the Mn–CH<sub>2</sub>  $\sigma$ -bond should be seen in the range of  $480\text{--}460\text{ cm}^{-1}$  [25], but they were not observed because of the low absorption coefficient of this band.

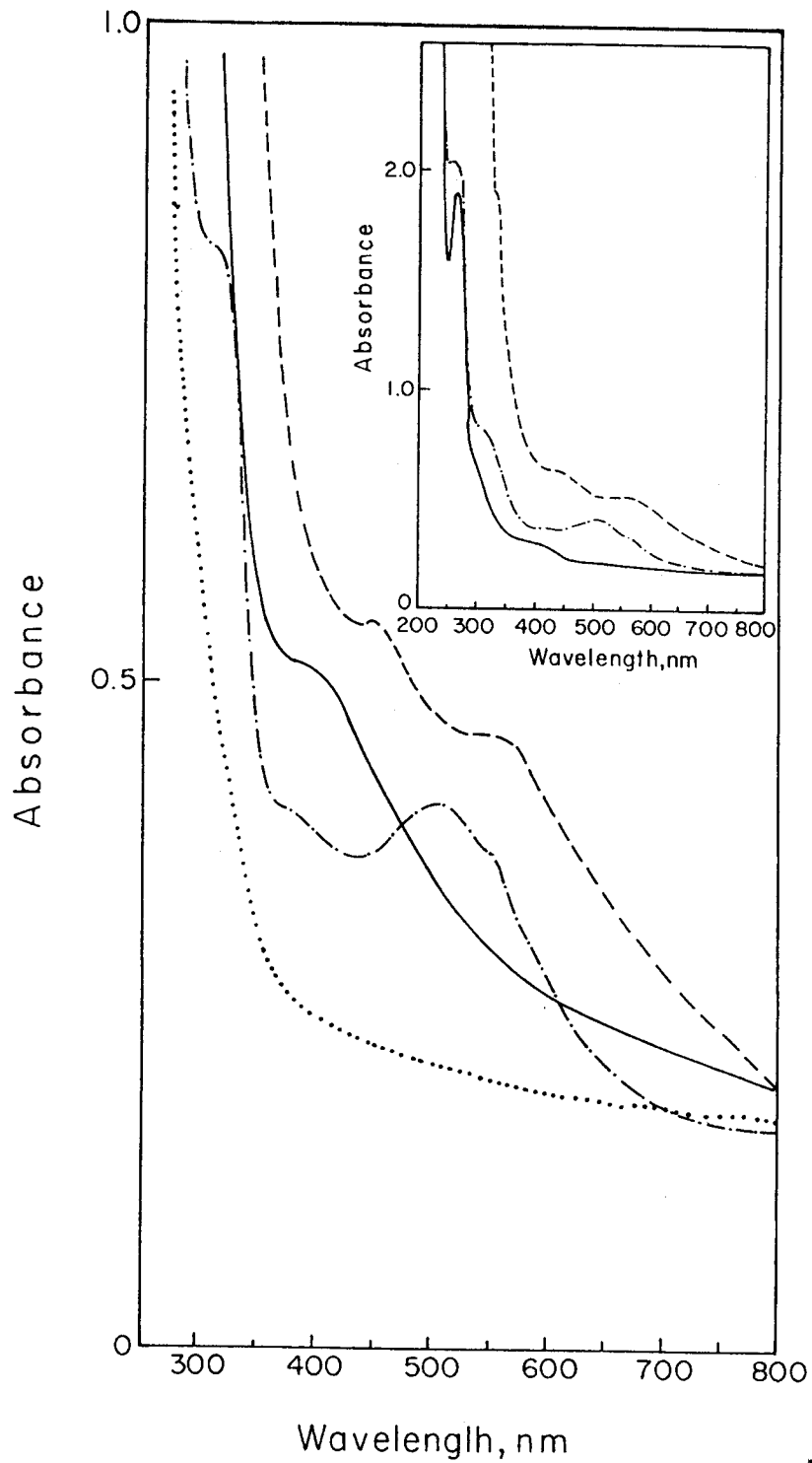
In addition to the ir bands of free PX and compound I, there are bands at  $1570$  and  $1160\text{ cm}^{-1}$  in the spectra of the PX–Mn cocondensated system. These bands are characteristic of disubstituted benzenes that contain groups in the para position with different Hammett constants [26]. Since the band at  $1600\text{ cm}^{-1}$  is absent in the spectra, there is no reason to assign the ir band at  $1570\text{ cm}^{-1}$  to a compound I structure. This band is

most likely related to the stretching vibrations of C=C bonds of the quinonoid structure in the weak  $\pi$ -complexes of PX-Mn. The band is shifted to a lower frequency compared to the analogous band of free PX (*viz.* 1590  $\text{cm}^{-1}$ ) owing to a partial electron transfer from Mn to the antibonding  $\pi$ -orbital of PX. Such low-frequency shifts of C=C and C-C stretching bands relative to those in the parent compounds are characteristics of  $\pi$ -bonded complexes [27]. The band at 1160  $\text{cm}^{-1}$  may be assigned to a symmetric in-plane vibration mode, including skeletal and C-H deformational vibrations of the quinonoid ring. The ir spectrum of free PX exhibits the same band but with a very low intensity. The higher band intensity is presumably due to bond polarization and breakdown of the PX symmetry in the complex. The other ir bands of the complex correlate with comparable bands of free PX. These  $\pi$ -complexes, which were not observed in the analogous Mg-PX system, result from the interaction of  $\pi$ -orbitals of PX with *d*-orbitals of Mn.

The difference between  $\sigma$  (compound I)- and  $\pi$ -bonded PX-Mn complexes is exhibited during the polymerization of the cocondensate. Under uv irradiation at 80 K the PX bands in the ir spectrum decrease sharply and the band of poly(PX) at 1510  $\text{cm}^{-1}$  appears (see Figs. 1a and b and 2a and b). As can be seen from the spectra (Fig. 2), polymerization is accompanied by destruction of the  $\pi$ -complexes: the bands at 1570  $\text{cm}^{-1}$  as well as those of free PX decrease sharply. The band at 1160  $\text{cm}^{-1}$ , which is related to the complexes, also decreases and is simultaneously shifted to a higher frequency. The reasons for this spectral shift are not yet clear; nevertheless, the observed effect indicates some kind of reorganization of the  $\pi$ -complexes during polymerization.

Photo-induced polymerization at 80 K does not lead to destruction of the  $\sigma$ -bonded organomanganese compounds: the intensity of the corresponding bands in the ir spectra is minimally affected by the polymerization. These compounds are incorporated into the poly(PX) chains, while the  $\pi$ -complexes are destroyed. The low-temperature organomanganese compounds in the polymerized system decompose after annealing to ambient temperature: all ir bands gradually disappear and the spectrum becomes identical to that of pure poly(PX) (Fig. 1c and 2c).

The uv-visible spectrum of the initial PX-Mn cocondensate shows absorption of high intensity in the short-wavelength region with a poorly resolved tail spreading up to 800 nm (Fig. 3). There is a weak band near 400 nm on the background of this absorption (Fig. 3, solid line). Irradiation of the cocondensate at 80 K results in the disappearance of this band and the growth of two new weak bands at 445 and 560 nm (Fig. 3, dashed line). This, together with the ir data discussed above, defines the band of the initial system at 400 nm as an intermolecular charge transfer band of



**Fig. 3.** The uv-visible spectra of the PX-Mn films with a Mn concentration of about 30 mol%. Solid line, original cocondensate at 80 K; dashed line, after uv irradiation at 80 K; dot-dash line, after annealing to room temperature; dotted line, after 24 h of storage at room temperature under vacuum.



the donor-acceptor  $\pi$ -complexes of PX with Mn. The band at 445 nm may be referred to as 0-0 electron transitions in stabilized terminal benzilic radicals of the polymer chains [28]. The main band of these radicals at 320 nm overlaps with the strong band of PX at 310 nm. It is suggested that the absorption near 560 nm is related to complexes of Mn with the radicals [28]. The band at 320 nm, which belongs to the polymer radicals, is seen in the spectrum of the room temperature annealed material because of polymerization of the residual monomer (Fig. 3, dot-dash line). In addition, the spectrum of the annealed material shows a long wavelength absorption with a maximum at 510 nm. Prolonged storage at ambient temperature under vacuum leads to a progressive decrease in both these bands and their eventual disappearance (Fig. 3, dotted line). We believe that the peak at 510 nm may also be related to the complexes of Mn with the polymer radicals. The shift of the band from 560 to 510 nm probably results from changes of the bonds between Mn and the radicals in the complex during annealing. By analogy with some previous results [29], the destruction of the organomanganese compounds and complexes under vacuum should lead to the formation of Mn clusters that have not been observed yet [29].

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