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Coordination Complexes between Iron(III) Chloride and Polyether, Polyester, and Poly(ether ester)[†]

J. F. Rabek,[*,‡] J. Lucki,[‡] B. J. Qu,[§] and W. F. Shi[§]

Department of Polymer Technology, Royal Institute of Technology, S100 44 Stockholm, Sweden, and China University of Science and Technology, Heifei, Anhui, China

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ABSTRACT: Poly(ethylene oxide) (poly(oxy-1,2-ethanediyl)), poly(β-propiolactone) (poly(2-oxetanone)), and poly(1,5-dioxepan-2-one) form coordination complexes with iron(III) chloride. The structures of these complexes have been studied with spectroscopic methods (UV–vis, FT-IR, Raman). Poly(ethylene oxide)–$FeCl_3$ complexes at polymer–$FeCl_3$ weight ratios of 9:1 and 8:2 give solid homogeneous phases which crystallize in the form of spherulites, whereas at ratios of 7:3 and 5:5 very highly viscous liquids are formed in which dendritic (7:3 complex) or needlelike (5:5 complex) crystals form. These crystals can be phase-separated low molecular weight species of $FeCl_3{\cdot}CH_3NO_2$ or $FeCl_3{\cdot}CH_3NO_2{\cdot}nH_2O$ rather than macromolecular crystals. All of these polymer–iron(III) chloride coordination complexes exhibit photochromic effects when they are exposed to UV (254 nm) radiation. However, polymers in these complexes are photodegraded in the $FeCl_3$ photoinitiated depolymerization reaction. Mechanisms of these photochromic and photodegradation reactions are discussed.

Introduction

Poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) can form coordination complexes with a number of metal salts, e.g., NaI, LiF, LISCN, NaSCN, and KSCN,[1–6] $ZnCl_2$, $ZnBr_2$, and ZnI_2,[7–11] $CaCl_2$,[12] $CoCl_2$,[8,10] $SnCl_2$,[10] $HgCl_2$, $HgBr_2$, HgI_2, and $CdCl_2$,[10,13–16] $FeCl_3$,[10] $LiClO_4$,[12,17–19] $LiBF_4$,[20] MoO_2Cl_2,[21] and Li, Na, and K phenolates and acrylates.[22] These coordination complexes, depending on the type of metal salt and polymer–metal salt weight ratio can give solid or single-phase thermoplastics. They can be applied as solid electrolytes in which the conduction arises from ionic migration as in the case of the PEO–NaI and PEO–$LiBF_4$.[23,24] The noncrystalline (amorphous) phase in these complexes has been considered to be the main pathway for ionic conduction.[2,25]

Coordination of polyethers has been most intensively studied with respect to the formation of single-phase thermoplastics. A common occurrence in these systems is the sharp increase in the glass transition temperature (T_g) by up to 140 °C by addition of metal chlorides.[8,10,11]

The good coordination properties of PEO for many salts are due to the optimal spacing of the heteroatom in the $-(CH_2CH_2O)-$ chain unit where the C–O bond length is 0.143 nm. When this geometry is changed, as in $-(CH_2O)-$ and $-(CH_2CH_2CH_2O)-$, the polymers have poor complexing properties for metal cations because of the incorrect spacing between O atoms. This highlights the point that a simple increase in polarity is insufficient to ensure good complexing characteristics.[18,26]

The polyester poly(β-propiolactone) (PPL) also forms a coordinate complex with $LiClO_4$ which exhibits an ionic conduction.[27] The spacing in PPL appears to be closer to the PEO requirements.

In these studies it was realized that not only poly(ethylene oxide) $-(CH_2CH_2O)-$ (PEO) but also the polyester poly(β-propiolactone) $-(CH_2CH_2COO)-$ (PPL) and the poly(ether ester) poly(1,5-di-oxepan-2-one) $-(CH_2CH_2OCH_2CH_2COO)-$ (PDXO), which all have a very similar structure, can form single-phase thermoplastics when complexed with $FeCl_3$ at a polymer–$FeCl_3$ weight ratio of 7:3. These complexes can initiate vapor-phase polymerization of pyrrole.[28]

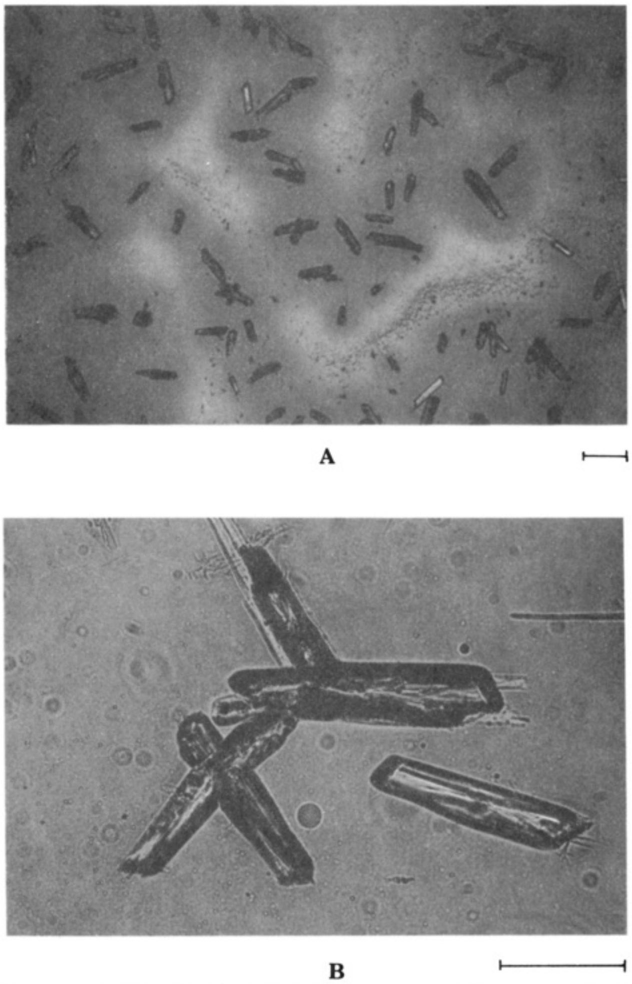

Figure 1. The $FeCl_3$–CH_3NO_2 complex existing as a highly viscous yellow liquid in which orthorhombic crystals are formed. Scale bars: (A) 100 μm; (B) 50 μm. (Photographs by J. F. Rabek.)

Experimental Section

A commercial poly(ethylene oxide) (poly(oxy-1,2-ethanediyl)) (PEO) (Type Polyox WSRN 750, M_w = 400 000, crystallinity ∼

[†] Dedicated to Professor Bengt Rånby on the occasion of his 70th birthday.

[‡] Royal Institute of Technology.

[§] China University of Science and Technology.

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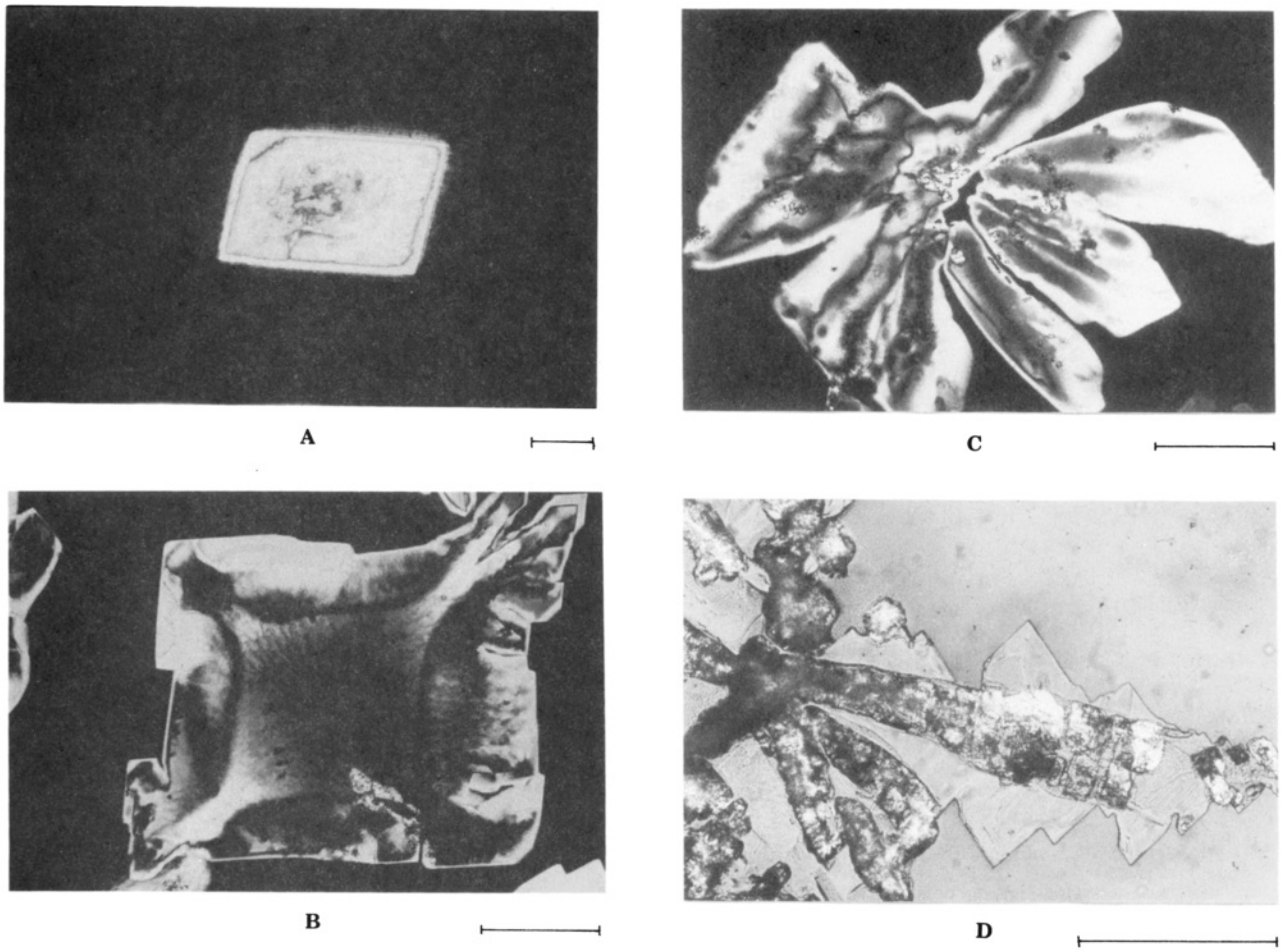

Figure 2. Successive stages of FeCl$_3$–CH$_3$NO$_2$ crystal formation: (A) orthorhombic crystal observed in the very early stage of crystallization; (B–D) successive stages of the dendrite form (D) formation. When the excess solvent evaporates, these dendrite forms (D) are decomposed into the orthorhombic crystals shown in Figure 1. Scale bars: (A) 50 μm; (B) 50 μm; (C) 50 μm; (D) 50 μm. (Photographs by J. F. Rabek.)

Table I
IR Spectra of PEO, PPL, PDXO, 7:3 PEO–FeCl$_3$, 7:3 PPL–FeCl$_3$, and 7:3 PDXO–FeCl$_3$

IR freq, cm^{-1}			IR freq, cm^{-1}			IR freq, cm^{-1}		
PEO	7:3 PEO–FeCl$_3$	assign	PPL	7:3 PPL–FeCl$_3$	assign	PDXO	7:3 PDXO–FeCl$_3$	assign
	1738	?	1725	1729	CO	1736	1728	CO
	1557	NO$_2$ (CH$_3$NO$_2$·FeCl$_3$)		1605	NO$_2$ (CH$_3$NO$_2$·FeCl$_3$)		1601	NO$_2$ (CH$_3$NO$_2$·FeCl$_3$)
1470	1470	CH$_2$ scissor	1460	1461	CH$_2$ scissor	1455	1444	CH$_2$ scissor
1460	1455	CH$_2$ scissor	1427	1396	CH$_2$ scissor	1392	1391	CH$_2$ scissor
1360	1353	CH$_2$ wag	1390		CH$_2$ scissor	1350	1372	CH$_2$ wag
1343		CH$_2$ wag	1373	1367	CH$_2$ wag	1325	1345	CH$_2$ wag
1281	1295	CH$_2$ twist	1354		CH$_2$ wag	1262	1284	CH$_2$ twist
1249	1249	CH$_2$ twist	1273	1284	CH$_2$ twist	1186	1191	CH$_2$ twist
1140		CH$_2$ twist	1171	1186	CH$_2$ twist	1127	1127	C–O, C–C
1112	1105	C–O, C–C	1075	1076	C–C, CH$_2$ rock	1071	1077	C–O, C–C, CH$_2$ rock
1062	1036	C–O, C–C, CH$_2$ rock	1013	1035	C–C, CH$_2$ rock	1040	1059	C–O, C–C, CH$_2$ rock
964	948	C–O, C–C, CH$_2$ rock	934		C–C, CH$_2$ rock	941	930	C–O, C–C, CH$_2$ rock
948		C–O, C–C, CH$_2$ rock	802	847	CH$_2$ rock	855	848	CH$_2$ rock
844	847	CH$_2$ rock				816	816	CH$_2$ rock

70–80%, produced by Union Carbide) was used without further purification.

The polyester poly(β-propiolactone) (poly(2-oxetanone)) (PPL) (M_w = 120 000, crystallinity ~ 60–75%) and the poly(ether ester) poly(1,5-dioxepan-2-one) (PDXO) (M_w = 10 000–50 000, noncrystalline polymer, highly viscous liquid) were synthesized and delivered in purified forms by Dr. T. Mathisen from our Department.[29-30]

Nitromethane (CH$_3$NO$_2$) (Carl Roth GmbH, Germany) was purified by vaccum distillation.

Anhydrous iron(III) chloride (FeCl$_3$) (Merck, Germany) was additionally purified by sublimation at 400 °C under a dry nitrogen atmosphere.

Polymer–FeCl$_3$ (PEO–FeCl$_3$, PPL–FeCl$_3$, and PDXO–FeCl$_3$) complexes were prepared by dissolving separately polymer (PEO, PPL, or PDXO) (5 wt %) and FeCl$_3$ (10 wt %) in dry nitromethane. These two solutions were mixed together and shaken for 30 min, cast on glass slides, and dried under a dry-nitrogen blanket.

DSC measurements were made with the Perkin-Elmer DSC 7 thermal analysis system.

UV–vis and IR spectra were recorded with Perkin-Elmer 575 UV–vis and FT-IR Perkin-Elmer 580B spectrometers, respectively. Polymer–FeCl$_3$ complex samples for spectral analysis were cast directly from solutions on a quartz cuvette (UV–vis) and NaCl plates (FT-IR), respectively.

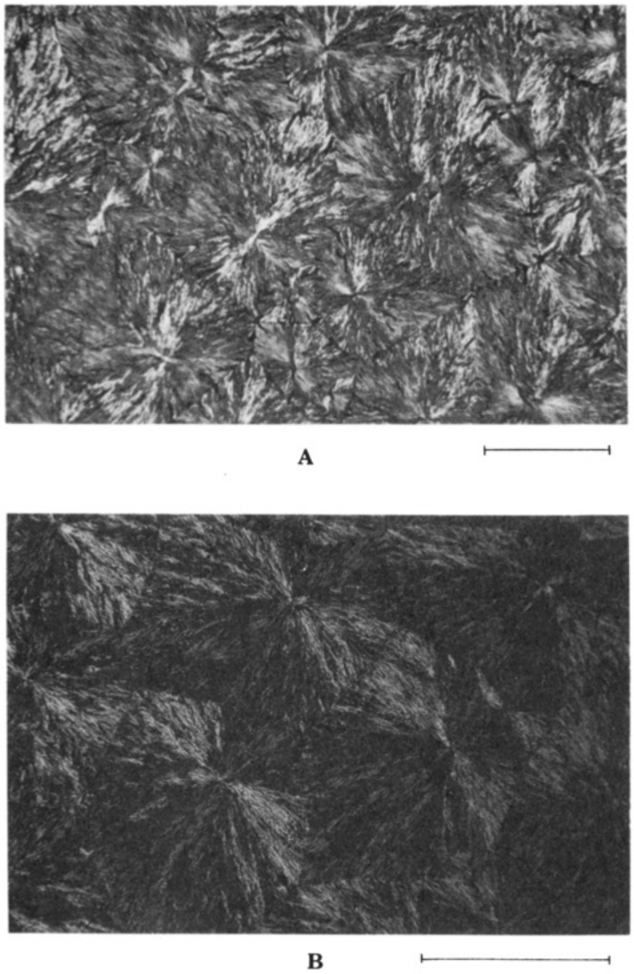

Figure 3. Photomicrographs of (A) poly(ethylene oxide) (PEO) spherulites (scale bar, 100 μm) and (B) PEO–$FeCl_3$ (8:2) complex spherulites (scale bar, 100 μm) made between crossed polarizers. (Photographs by J. F. Rabek.)

Laser Raman spectra were recorded with a SPEX 1403 laser Raman spectrometer using 5145-Å excitation wavelength.

Photochromic and photodegradation reactions were initiated with a UV HPK 125-W (Philips) low-pressure lamp.

Photomicrographs were made with the Leitz Ortholux II POL-BX microscope and Olympus camera using Ektachrome 100 HC (100 DIN) films.

Results and Discussion

The black crystalline $FeCl_3$ has a semicovalent layer structure in which each iron atom is octahedrally surrounded by chlorine. Iron(III) chloride forms solvates with many nonaqueous solvents (solvate complexes), e.g., $FeCl_3{\cdot}2C_2H_5OH$[31,32] and $FeCl_3{\cdot}(C_2H_5)_2O$,[32] or addition complexes with benzene,[33] dimethyl sulfoxide,[31] *N*-methylacetamide,[31] and *N*,*N*-dimethylacetamide.[34] The structures of many of these complexes are still unknown. According to the coordination model, these solvates and addition complexes can form some equilibrate, during which a number of ionic species can be formed according to the reactions[31,34]

$$FeCl_3(\text{solid}) + S\ (\text{solvent}) \rightarrow (FeCl_3S_n)_x \rightleftharpoons FeS_4Cl_2^{\ +} + FeCl_4^{\ -} \quad (1)$$

$$FeS_4Cl_2^{\ +} + S \rightleftharpoons FeS_5Cl^{2+} + Cl^- \quad (2)$$

$$FeS_5Cl^{2+} + S \rightleftharpoons FeS_6^{\ 3+} + Cl^- \quad (3)$$

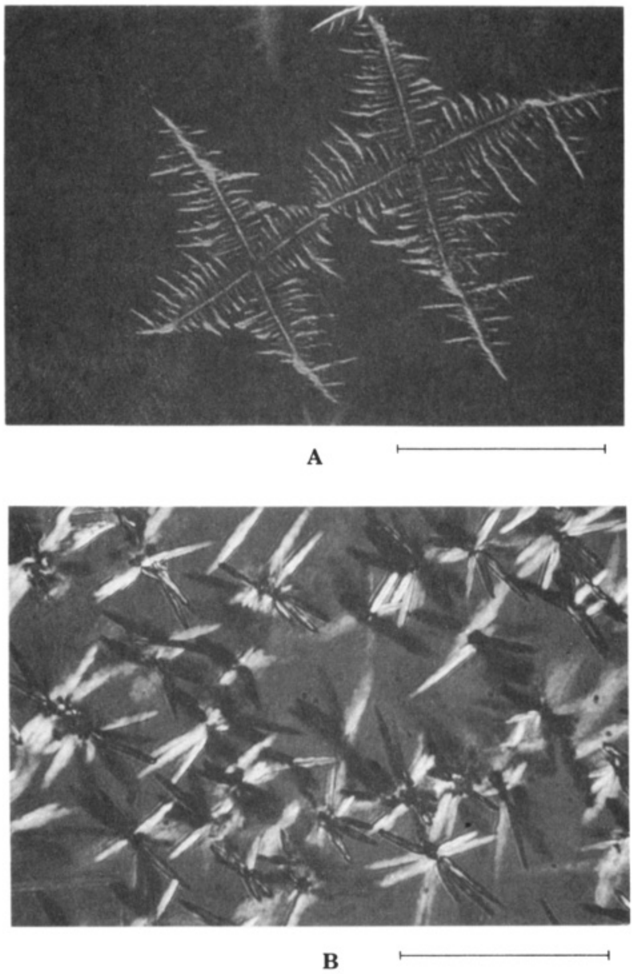

Figure 4. (A) Photomicrograph of dendritic crystals formed in the amorphous poly(ethylene oxide) (PEO)–$FeCl_3$ (7:3) complex (scale bar, 100 μm) made between crossed polarizers. (B) Photomicrograph of needlelike crystals formed in the amorphous poly(ethylene oxide) (PEO)–$FeCl_3$ (5:5) complex (scale bar, 50 μm) made between crossed polarizers. (Photographs by J. F. Rabek.)

The number of solvent molecules coordinated to a cation is not known. The tetrachloroferrate ion ($FeCl_4^-$) is strongly yellow colored and has two strong absorption bands at ca. 320 and 360 nm ($\epsilon = 10^3$–10^4 L mol^{-1} cm^{-1}). The formation of the tetrachloroferrate ion has also been observed in polymer matrices such as poly(vinyl chloride),[35] poly(acrylic acid),[36] and poly(methyl methacrylate),[37] where $FeCl_3$ forms strong charge-transfer complexes with polymer molecules.

Iron(III) chloride dissolved in nitromethane is partially solvated; however, it can also form a strongly colored addition complex in which tetrachloroferrate ion ($FeCl_4^-$) is formed, probably by the disproportionation process given by the equation

$$nS\ (\text{nitromethane}) + 2Fe^{3+}(Cl^-)_3 \rightarrow S_n(Fe^{3+}(Cl^-)_2)^+(Fe^{3+}(Cl^-)_4)^- \quad (4)$$

After evaporation of the excess solvent, $FeCl_3$–CH_3NO_2 addition complex exists as a highly viscous yellow liquid in which orthorhombic crystals are formed (Figure 1). In the very early stages of crystallization, dendritic crystalline structures are formed (Figure 2), which then disappear as the solvent evaporates.

Poly(ethylene oxide) (PEO) dissolved in nitromethane and mixed with a solution of $FeCl_3$ (in nitromethane) forms strongly yellow colored complexes. Depending on the

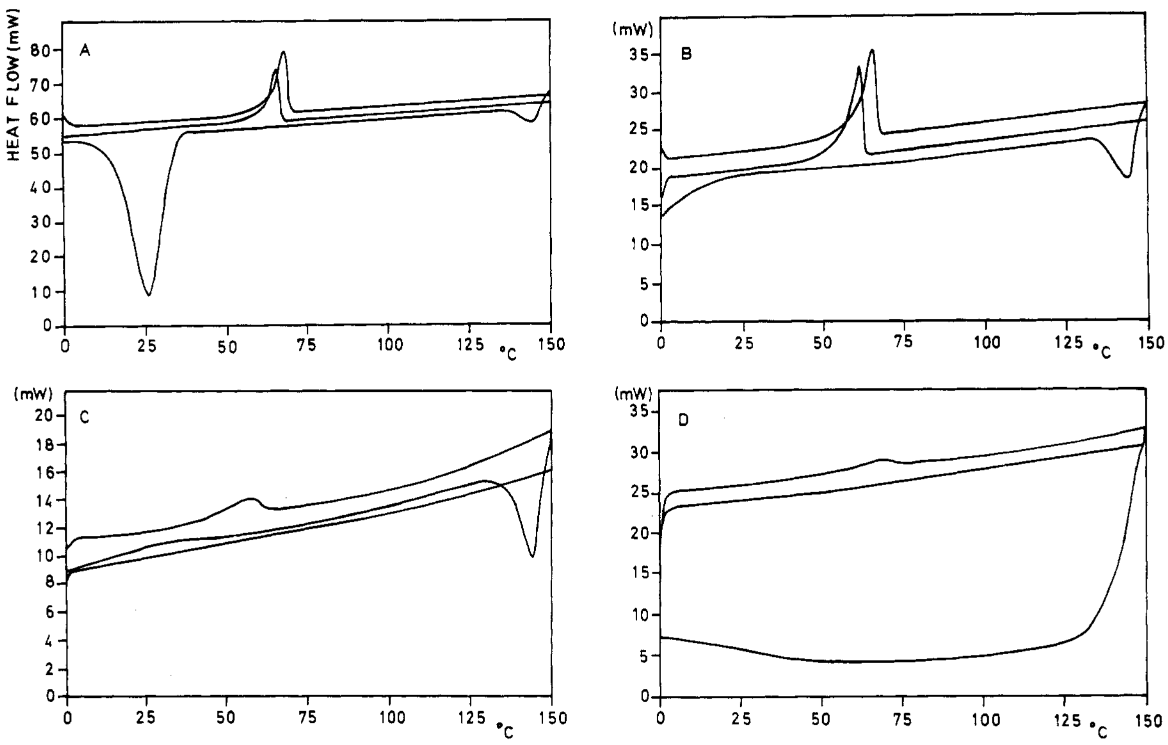

Figure 5. DSC curves for (A) pure PEO crystallized from nitromethane solution (5 wt %), (B) 9:1 PEO-FeCl$_3$, (C) 7:3 PEO-FeCl$_3$, and (D) 5:5 PEO-FeCl$_3$.

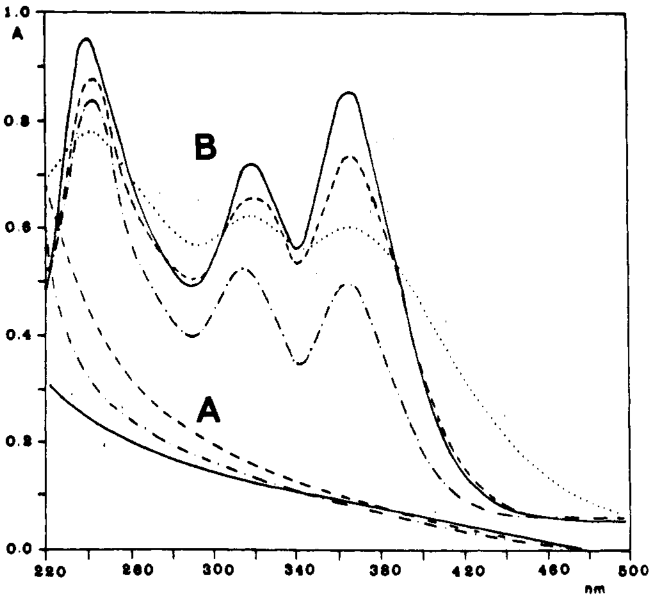

Figure 6. UV-vis absorption spectra of (A) (—) PEO, (-·-) PPL, and (- - -) PDXO and (B) (···) FeCl$_3$-CH$_3$NO$_2$, (—) 7:3 PEO-FeCl$_3$, (-·-) 7:3 PPL-FeCl$_3$, and (- - -) 7:3 PDXO-FeCl$_3$.

PEO/FeCl$_3$ weight ratio, these complexes can be solid or highly viscous single-phase liquids. At a PEO/FeCl$_3$ weight ratio of 9:1 or 9:2, solid-state complexes are formed, having well-developed spherulite structures (Figure 3B) similar to those observed in the original PEO which was crystallized from nitromethane (Figure 3A). These complexes are very homogeneous, and no phase separation is observed between PEO and FeCl$_3$. However, at a PEO/FeCl$_3$ weight ratio of 7:3 or 5:5, single-phase, highly viscous, strongly yellow colored liquids are formed. Depending on the PEO/FeCl$_3$ weight ratio in these liquids, dendritic (at PEO/FeCl$_3$ = 7:3) (Figure 4A) or needlelike, whisker-type crystals (at PEO/FeCl$_3$ = 5:5) (Figure 4B) are formed. However, the dendritic crystals formed at PEO/FeCl$_3$ = 7:3 (Figure 4A) must originate from the crystallization on the dendritic forms observed during the crystallization of the FeCl$_3$-CH$_3$NO$_2$ solution (Figure 2). These dendrites disappear upon warming the sample to 48 °C (recrystallization at 42 °C) and also during UV (254 nm) irradiation and in a constant electric field of 24 V when two electrodes were attached to both sides of a sample.

The DSC measurements made in the region 0–150 °C are shown in Figure 5. The pure PEO recrystallized from nitromethane (Figure 5A) shows that the spherulite structures melt in the region 52–75 °C, which is in good agreement with the melting process observed under the polarizing microscope. A broad endotherm with T_{max} at 26 °C is due to the crystallization process of PEO. Complexes of PEO with FeCl$_3$ (Figure 5B–D) do not show this endothermic event. Small exothermic peaks observed in the 7:3 PEO-FeCl$_3$ (Figure 5C) and 5:5 PEO-FeCl$_3$ complexes (Figure 5D) are due to the melting dendritic (Figure 4A) and needlelike structures (Figure 4B), respectively. The DSC curves for all PEO-FeCl$_3$ complexes are different from the DSC curve for pure PEO.

The dendrites (Figure 4A) and needles (Figure 4B) can be phase-separated, low molecular weight species of FeCl$_3$·CH$_3$NO$_2$ or FeCl$_3$·CH$_3$NO$_2$·nH$_2$O (water from the air) and their melting temperatures can lie in the region of 50–70 °C. For example, FeCl$_3$·6H$_2$O has the melting temperature 37 °C. Furthermore, it is to be expected that the low molecular weight species should dissolve in a highly solvolytic medium such as PEO at a temperature below the melting temperature of the pure salt (for FeCl$_3$ the melting temperature is 282 °C). However, the dendrites and needles can also have more complicated structures in which PEO-FeCl$_3$-CH$_3$NO$_2$ molecules are involved. The IR spectra of these structures in the region 4000–600 cm^{-1} are almost identical with those of the amorphous phase of PEO-FeCl$_3$ complexes. The structures of these crystals have not been determined in detail.

The polyester poly(β-propiolactone) (PPL) and the poly(ether ester) poly(1,5-dioxepan-2-one) (PDXO) also form

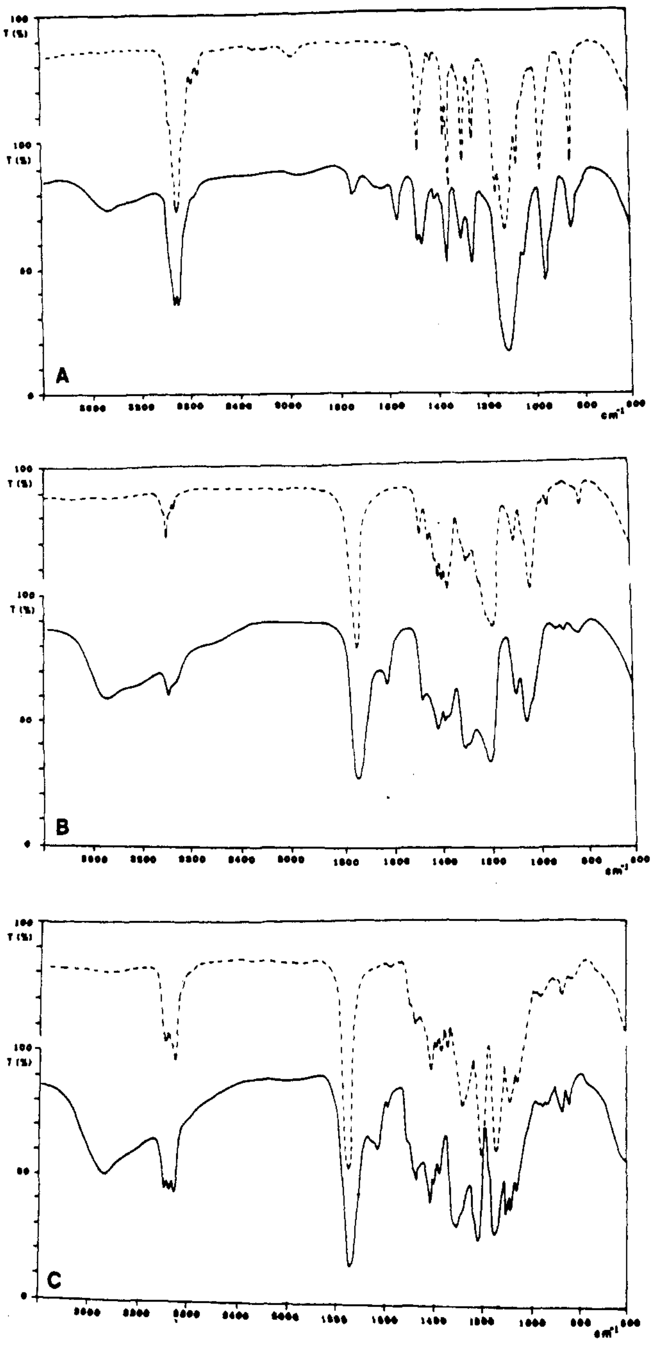

Figure 7. IR absorption spectra of (A) (- - -) PEO and (—) 7:3 PEO–FeCl$_3$, (B) (- - -) PPL and (—) 7:3 PPL–FeCl$_3$, and (C) (- - -) PDXO and (—) 7:3 PDXO–FeCl$_3$.

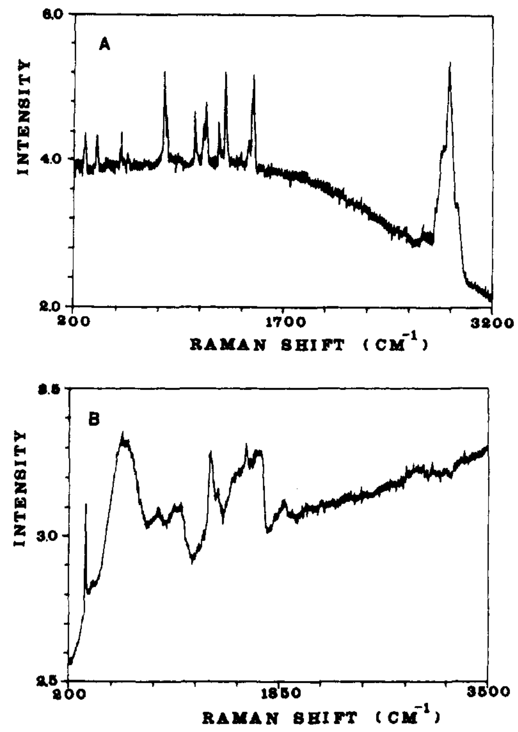

Figure 8. Raman specrra of (A) PEO and (B) 7:3 PEO–FeCl$_3$ complex.

single-phase, highly viscous addition complexes with FeCl$_3$ at a weight ratio of 7:3. However, in these liquids formation of any crystalline forms has not been observed.

All three of these polymer–FeCl$_3$ complexes (PEO–FeCl$_3$, PPL–FeCl$_3$, and PDXO–FeCl$_3$) have very strong absorption in the range 220–400 nm, with two characteristic absorption bands at 320 and 360 nm (Figure 6). This is attributed to the formation of the tetrachloroferrate ion (FeCl$_4^-$) which is similar to that observed in FeCl$_4$–CH$_3$NO$_2$ and other addition complexes.[31,34]

Infrared spectra of these polymer–FeCl$_3$ (PEO–FeCl$_3$, PPL–FeCl$_3$, and PDXO–FeCl$_3$) complexes (Figure 7) show an increase in the number of absorption bands over the original polymers and large frequency shifts due to strong interactions between polymer chains and FeCl$_3$ (Table I).

These changes in the IR spectra of the PEO–FeCl$_3$ complex are consistent with the chain adopting trans (CCOC), gauche (OCCO), and trans (COCC) conformations.[38–40] These conformations allow the formation of five-membered rings along the chain formed from two carbon atoms, two oxygen atoms, and the metal atom. An increase in the number of absorption bands over the original polymer can be explained as a result of the formation of the gauche from the trans conformation. The PEO in the crystalline state has a helical structure consisting of a succession of nearly trans, trans, and gauche forms about the C–O, O–C, and C–C bonds, respectively.[40–43] The change of PEO conformation in the complex with HgCl$_2$ gives the conformation T$_5$GT$_5\bar{\mathrm{G}}$, where G and $\bar{\mathrm{G}}$ denote the right- and left-handed gauche forms, respectively.[44]

The formation of five-membered rings in PEO–metal salt complexes may be used to quantitatively explain the observed elevation of T_g.[8,10,11] The polymer chain may be considered to be a random copolymer consisting of uncoordinated and coordinated monomer units. Unchelated oxygen atoms may still coordinate, however, and FeCl$_3$ molecules may act either as cross-links between chains or simply as side groups on the chain. At very high FeCl$_3$ concentrations all available oxygen atoms are complexed, and the stabilization of a molecular dispersion of further salt molecules by coordination becomes impossible.

In all polymer–FeCl$_3$ (PEO–FeCl$_3$, PPL–FeCl$_3$, and PDXO–FeCl$_3$) complexes, the IR spectra (Figure 7) show the large frequency shift (Table I) due to the strong complex formation between these polymers and FeCl$_3$. A similar IR frequency shift has been observed in a number of polymers such as poly(vinyl acetate), poly(vinyl alcohol), poly(methyl methacrylate), poly(methyl acrylate), and cellulose acetate with certain inorganic nitrate salts which are quite soluble in these polymers.[45] In the case of PEO–FeCl$_3$, PPL–FeCl$_3$, and PDXO–FeCl$_3$ complexes, it is probable that only one type of complex is formed, because the polymer bands that shift are almost always from the same structures, namely, C–O and C–C (CH$_2$) groups. The IR shifts observed in the IR spectra make it evident that the partially negatively charged ether oxygens act as

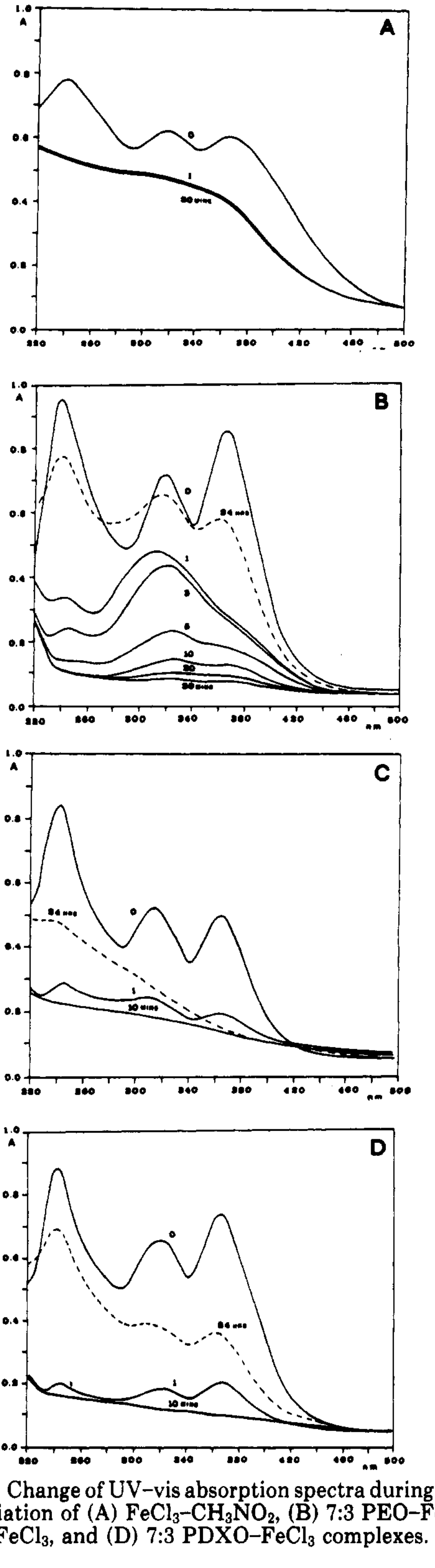

Figure 9. Change of UV–vis absorption spectra during UV (254 nm) irradiation of (A) $FeCl_3$–CH_3NO_2, (B) 7:3 PEO–$FeCl_3$, (C) 7:3 PPL–$FeCl_3$, and (D) 7:3 PDXO–$FeCl_3$ complexes.

ligands for the metal ion in the complex. The ether (C–O) frequency moves to higher energy, apparently because of an increase in bond order for the ether linkage. The metal ion undoubtedly has its Cl^- counterions nearby, and the cation is probably still solvated by nitromethane (and traces of water absorbed from the surrounding atmosphere). In general, only the original polymer structure and the complex are present, with no other structures existing. This is indicated by the discrete shift in frequency in the polymer spectra rather than in a gradual shift as a function of salt concentration. Each polymer (PEO, PPL, or PDXO) segment molecule is coordinated differently, depending on its interaction with the $FeCl_3$–CH_3NO_2 complex. This complex exhibits strong absorption bands at 1470 (PEO), 1605 (PPL), and 1601 (PDXO) cm^{-1}, which belong to the NO_2 group in the $FeCl_3$–CH_3NO_2 complex. Pure CH_3NO_2 shows the following IR bands: asymmetric stretching (ν_{NO_2}(asym)) at 1562 cm^{-1}, symmetric stretching (ν_{NO_2}(sym)) at 1384 cm^{-1}, scissoring deformation (δ_{ONO}) at 647 cm^{-1}, and bending (ρ_{NO_2}) at 599 and 476 cm^{-1}. However, in the region 1630–1600 cm^{-1} there exists also an H–O–H bending mode. $FeCl_3 \cdot nH_2O$ exhibits a strong absorption band at 1620 cm^{-1}.

It is evident that the Raman spectrum of pure PEO (Figure 8A) differs from that of the PEO–$FeCl_3$ complex (Figure 8B). In pure PEO, the methylene groups (CH_2's) display five types of vibrations with the following band positions: asymmetric stretching (ν_{CH}(asym)) at 2880–2900 cm^{-1}, symmetric stretching (ν_{C-H}(sym)) at 2842 cm^{-1}, scissoring deformation (δ) at 1480 cm^{-1}, wagging deformation (ω) at 1282 cm^{-1}, and carbon chain deformation vibrations in the range 600–200 cm^{-1} (278, 362, and 534 cm^{-1}).[40] The C–O–C grouping can vibrate symmetrically and asymmetrically. Since the atomic mass of a carbon atom differs only slightly from that of oxygen and the force constants are close in value, both symmetrical and asymmetrical vibrations are strongly coupled with the remaining skeletal vibrations. The asymmetric stretching vibrations (ν_{C-O}(asym)) lie at 1064, 1126, and 1140 cm^{-1}, whereas symmetric stretching vibrations (ν_{C-O}(sym)) are at 846 and 880 cm^{-1}. In a macromolecule, the intramolecular vibrations are strongly affected by the polymer chain conformation. In crystalline PEO there are two additional bands at 1234 and 1394 cm^{-1}, which are probably associated with crystal lattice vibrations. In the Raman spectrum of the PEO–$FeCl_3$ complex (Figure 8B), methylene group stretching vibrations at 2800–2900 cm^{-1} disappear completely, whereas carbon chain deformation bands at 600–200 cm^{-1} are replaced by a strong broad band with a maximum at 620 cm^{-1}. The 534- and 584-cm^{-1} bands are associated with the CCOC and COCC bending mode of the C–O band in the solid state and can be assigned to the trans–trans structure of the successive C–O bond. The formation of a broad band with a maximum at 620 cm^{-1} is probably associated with the trans–gauche or gauche–gauche structures of the successive C–O–C bond chelated to the Fe atom. It is very clear that in the 7:3 PEO–$FeCl_3$ complex, the helix structure of PEO is destroyed, and new rotational isomers are observed. There is also a strong change in the C–O–C group vibrations at 800–1200 cm^{-1}. Two broad bands are formed at 875 and 1025 cm^{-1}, where the stretching vibrations are located. This change indicates strong interaction of the n electrons of the ether group in PEO with the $FeCl_2^+$ cation in a charge-transfer coordination complex. The scissoring and wagging deformation bands (1480 and 1282 cm^{-1}, respectively) are replaced by new strong bands at 1685 and 1305 cm^{-1}. This also indicates a change from a helical structure to a new, less ordered but not completely disordered structure in the PEO–$FeCl_3$ complex. Information collected from IR and Raman spectra does not allow, without the support of WAXS and SAXS, for the determination of the PEO–$FeCl_3$ complex structure.

Under UV (254 nm) irradiation, these polymer–$FeCl_3$ (PEO–$FeCl_3$, PPL–$FeCl_3$, and PDXO–$FeCl_3$) complexes are bleached and their UV–vis absorption spectra decrease (Figure 9). However, the yellow color and absorption spectra are partially restored in the dark after 24 h. This effect has not been observed in the case of UV irradiation of the $FeCl_3$–CH_3NO_2 complex (Figure 9A). A similar photochromic effect has been previously observed in poly(vinyl chloride)–$FeCl_3$[35] and poly(methyl methacrylate)–$FeCl_3$[37] upon UV irradiation. This photochromic effect is a result of the photoreduction of $FeCl_4^-$ due to a rapid electron exchange in the ion pair $FeCl_2^+\cdots FeCl_4^-$ generated by UV irradiation:[46]

$$(FeCl_2^+\cdots FeCl_4^-) \xrightarrow{+h\nu} (FeCl_2^{\bullet+}\cdots FeCl_3^-) + Cl^\bullet \qquad (5)$$

$$(FeCl_2^{\bullet+}\cdots FeCl_3^-) \xrightarrow{\text{dark}} FeCl^{\bullet+} + FeCl_4^- \qquad (6)$$

$$FeCl^{\bullet+} + Cl^\bullet \xrightarrow{\text{dark}} FeCl_2^+ \qquad (7)$$

The polymer complex matrices play an important role for the mobility of ion pairs in them and subsequently for the kinetics of photochromic reactions (Figure 9).

In poly(vinyl chloride)–$FeCl_3$, the photochromic effect has only been observed in the presence of air (oxygen).[35] Oxygen participates probably in the following reactions:

$$FeCl^{\bullet+} + O_2 \rightarrow FeCl^{2+} + O_2^{\bullet-} \qquad (8)$$

$$O_2^{\bullet-} + HCl \rightarrow HO_2^\bullet + Cl^- \qquad (9)$$

$$FeCl^{2+} + Cl^- \rightarrow FeCl_2^+ \qquad (10)$$

$$FeCl_2^+ + FeCl_4^- \rightarrow (FeCl_2^+\cdots FeCl_4^-) \rightleftharpoons 2FeCl_3 \qquad (11)$$

The HCl is produced from the photodecomposition of poly(vinyl chloride).

UV irradiation causes parallel $FeCl_3$-photoinitiated degradation of PEO, PPL, and PDXO polymers. IR spectra (Figure 10) show that this process is mainly depolymerization (decreasing intensity of most absorption bands in the region 1800–800 cm^{-1}). It is accompanied, however, by photooxidative reactions (formation of a strong band at 3450 cm^{-1} attributed to the formation of OOH/OH groups and a band at 1720 cm^{-1} assigned to the CO group).

The photolysis (photoreduction) of iron(III) chloride complexes occurs with formation of chlorine atoms (radicals) by the following reactions:

$$Fe^{3+}(Cl^-)_n \overset{+h\nu}{\rightleftharpoons} Fe^{2+}(Cl^-)_{n-1}\cdots Cl^\bullet \rightarrow Fe^{2+}(Cl^-)_{n-1} + Cl^\bullet \qquad (12)$$

where n is the number of chlorine atoms in the initial complex chlorine radical ($Cl^\bullet$), which may further abstract hydrogen from the methylene (CH_2) groups in the PEO, PPL, or PDXO polymers (PH):

$$PH + Cl^\bullet \rightarrow P^\bullet + HCl \qquad (13)$$

The polymer alkyl radicals ($P^\bullet$) can then react with oxygen to form polymer alkylperoxy radicals ($POO^\bullet$), which produce hydroperoxy groups (OOH at 3450 cm^{-1}) and carbonyl groups (CO at 1720 cm^{-1}) (by the β-scission process).

The Fe^{2+} can be oxidized to Fe^{3+} with the help of polymer alkyl radicals ($P^\bullet$) according to the following reactions:[47]

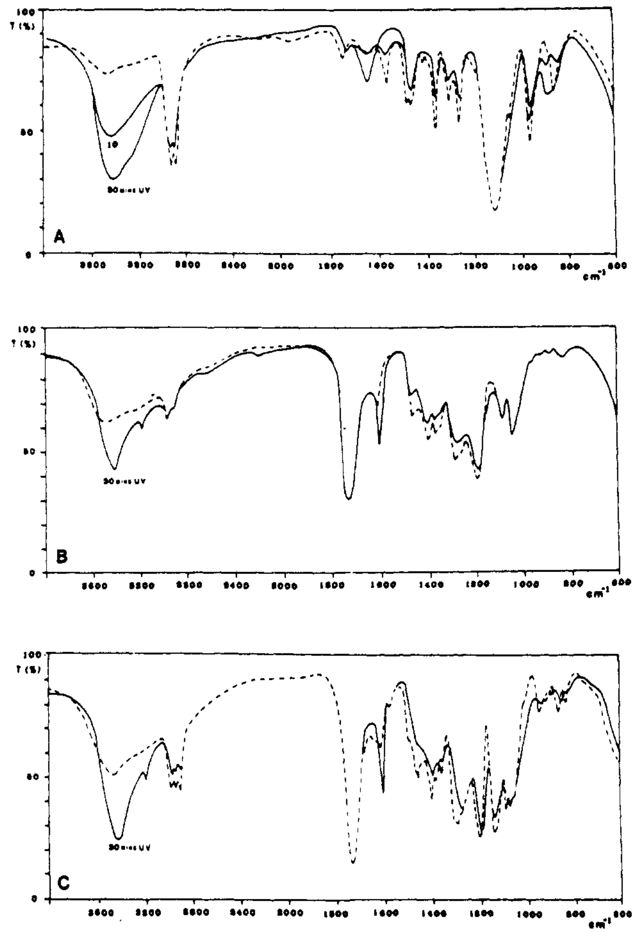

Figure 10. Change of IR absorption spectra during UV (254 nm) irradiation of (A) 7:3 PEO–$FeCl_3$, (B) 7:3 PPL–$FeCl_3$, and (C) 7:3 PDXO–$FeCl_3$ complexes: (- - -) before irradiation; (—) after irradiation.

$$Fe^{2+}(Cl^-)_{n-1} + P^\bullet \rightarrow Fe^{3+}(Cl^-)_{n-1} + P^- \qquad (14)$$

$$P^- + HCl \rightarrow PH + Cl^- \qquad (15)$$

$$Fe^{3+}(Cl^-)_{n-1} + Cl^- \rightarrow Fe^{3+}(Cl^-)_n \qquad (16)$$

The above reactions can fully explain the observed photochromic effect and the photodegradation of PEO–$FeCl_3$, PPL–$FeCl_3$, and PDXO–$FeCl_3$. efficiency of photodegradation of these complexes is low ($\phi < 10^{-3}$), probably because most of the UV irradiation absorbed is consumed for reactions involved in the photochromic processes.

On the other hand, transition-metal ions of variable valence easily form complexes with hydroperoxide (OOH) groups, which are photodecomposed under UV irradiation with formation of polymer peroxy ($POO^\bullet$) and/or polymer oxy ($PO^\bullet$) radicals:[48]

$$Fe^{3+} + POOH \rightleftharpoons (Fe^{3+}\cdots HOOP) \text{ (complex)} \qquad (17)$$

$$(Fe^{3+}\cdots HOOP) \rightleftharpoons Fe^{2+} + POO^\bullet + H^+ \qquad (18)$$

$$Fe^{2+} + POOH \rightleftharpoons (Fe^{2+}\cdots HOOP) \text{ (complex)} \qquad (19)$$

$$(Fe^{2+}\cdots HOOP) \rightleftharpoons Fe^{3+} + PO^\bullet + OH^- \qquad (20)$$

$$H^+ + OH^- \rightarrow H_2O \qquad (21)$$

All reactions in which polymer alkyl ($P^\bullet$), polymer oxy ($PO^\bullet$), and polymer peroxy ($POO^\bullet$) radicals are formed may influence the photochromic mechanism and decrease the observed effect.

Conclusion

These results indicate that not only PEO but also PPL and PDXO form coordination complexes with $FeCl_3$. Under UV irradiation, PEO-$FeCl_3$, PPL-$FeCl_3$, and PDXO-$FeCl_3$ complexes show a photochromic effect, accompanied by a slow photodegradation process. According to the coordination model, the main ionic species in these complexes is tetrachloroferrate ion ($FeCl_4^-$), which is responsible for the photochromic effect. In the PEO-$FeCl_3$ complex, very interesting spherulitic, dendritic, and needlelike crystals are formed. Further research on these complexes is underway.

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