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(42) We are aware of two factors which can affect the initial rate of the acid consumption in the system involving the cyclic monomers. The initial product of the ring opening, which has $\equiv$SiOSi$\equiv$ groups, may undergo some fast fragmentations, allowing for the introduction of more acid. On the other hand, the propagation, which is fast in comparison with the initiation, is accompanied by end-to-end ring closure in which some of the acid is regenerated.[10,11] Similar complications may arise in DXL acidolysis; this process is being further studied at our Center.
(43) The ester of acetic acid is not formed in appreciable amount, as found by ^{1}H NMR.
(44) It is our feeling that the role of water as proton donor to the monomer is most important.

Rare Earth Metal Containing Polymers. 3. Characterization of Ion-Containing Polymer Structures Using Rare Earth Metal Fluorescence Probes[1a]

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ABSTRACT: Eu^{3+}, Tb^{3+}, and Co^{2+} salts of polymers containing carboxylic acid and sulfonic acid ligands were prepared and characterized. The polymers investigated were poly(acrylic acid) (PAA), copolymers of styrene–acrylic acid (PSAA), styrene–maleic acid (PSM), and methyl methacrylate–methacrylic acid (PMM/MA), and partially carboxylated and sulfonated polystyrenes (CPS and SPS). The lanthanide salts of these polymers showed characteristic lanthanide ion fluorescence in the solid state on excitation with UV light. The fluorescence excitation and emission spectra of these salts excepting carboxylated polystyrene showed characteristic spectra of the free ions, indicating that no energy is transferred from the polymer matrix to the ions. The carboxylated polystyrene–Eu^{3+} and –Tb^{3+} showed broad excitation spectra similar to the spectrum of the polymer and emission from the lanthanide ions, suggesting energy transfer from the polymer to the ion. The fluorescence intensities of the lanthanide salts of PAA, PSM, CPS, and SPS were found to increase linearly with the metal ion content. However, the salts of PSAA and PMM/MA displayed typical fluorescence concentration quenching behavior, reaching a maximum at 4–6 wt % of metal and decreasing with further increases in metal content. These results suggest that PSAA and PMM/MA contain ionic aggregates in which Eu and Tb ions are located close together. The energy transfer from Tb^{3+} to Co^{2+} and Eu^{3+} was evaluated from the Tb^{3+} fluorescence quenching. This was much more efficient in PSAA than in CPS and SPS systems. These results confirm that ion aggregates exist in PMM/MA and PSAA but not in the CPS and SPS systems at low metal concentration (<6 mol %). The probability $P_{D\rightarrow A}$ of dipole–dipole transfer between Tb^{3+} and Co^{2+} statistically distributed in a polymer matrix and the quenching characteristics were calculated by using Förster's equation. Experimental fluorescence quenching behaviors for PASS, CPS, and SPS are discussed as compared with the calculated quenching curve.

Introduction

The structures of synthetic polymers containing metal ions have been extensively investigated in recent years.[2,3] A host of techniques, including small-angle X-ray scattering, electron microscopy, and Raman spectroscopy, have been brought to bear on the elucidation of the structures of ion-containing polymers. It has been proposed that certain polymers contain submicroscopic aggregations of ionic groups.[3,4] Various structures of the ionic aggregates have been proposed and these depend on the composition of polymers, nature and concentration of metal ions, temperature, etc.

In the arsenal of spectroscopic techniques, fluorescence measurements offer particular advantages since they are sensitive and can be employed at relatively low concentrations of the luminescent species.[5] Thus, we have initiated a study of the structures of ion-containing polymers, using trivalent lanthanide ions as fluorescent probes.

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Table I

PSAA sample[a]	feed, mol % styrene	feed, mol % acrylic acid	found, mol % styrene	found, mol % acrylic acid	polymer obtained %
I	90	10	87	13	10
II	90	10	91	9	69

[a] PSAA I may be homogeneous; PSAA II is a rather heterogeneous copolymer.

The fluorescence intensity of samples containing uniformly dispersed europium(III) acetate in polystyrene or poly(methyl methacrylate) was found to increase linearly with Eu content. However, the Eu^{3+} salts of copolymers of methyl methacrylate–methacrylic acid and styrene–acrylic acid displayed typical concentration quenching behavior, reaching a maximum at 3–5 wt % Eu and decreasing with further increases in Eu content.[6] This result shows that the ion-containing polymers contain ionic aggregates, in agreement with a recently proposed model. Such aggregates would create locally high Eu ion concentrations, whose interactions lead to concentration quenching at low overall Eu concentrations.

In this paper, the fluorescence technique was further applied to elucidate ion aggregate formation in various ion-containing polymers. We also studied the distances between metal ions in these polymers, using Tb^{3+}–Eu^{3+} and Tb^{3+}–Co^{2+} energy transfer as metal–metal distance probes.

Experimental Section

Materials. Polymers. Copolymers of Styrene–Acrylic Acid (PSAA), Styrene–Maleic Acid (PSM), and Methyl Methacrylate–Methacrylic Acid (PMM/MA). PMM/MA was obtained by partial hydrolysis of PMMA with NaOH in 2-propanol solution.[6] The acid content of PMM/MA obtained was determined by titration and found to be 6.8 mol %.

Two different PSAA samples prepared under the conditions in Table I were used and the copolymers' composition was determined by UV absorption and by titration.[6]

Poly(acrylic acid) was obtained from Polysciences Inc. Two samples of the sodium salt of sulfonated polystyrenes (SPS) (sodium sulfonate contents 2.6 and 6.1 mol %) were supplied by Dr. H. S. Makowski, Exxon Research and Engineering Co. Two carboxylated polystyrenes (CPS) were used. One of the polymers (sodium carboxylate, 6.4 mol %) was obtained from Dr. R. D. Lundberg, Exxon Research and Engineering Co. Another polymer was prepared in our laboratory by the method described in the literature.[7] Polystyrene (Polysciences Inc., MW = 20 000) was used and the carboxylic acid content in the polymer synthesized was found to be 4.6 mol %.

Lanthanides. Europium chloride ($EuCl_3 \cdot 6H_2O$) and terbium chloride ($TbCl_3 \cdot 6H_2O$) were purchased from Ventron Co. These chlorides were used without further purification. Europium acetate was synthesized by the method described in the literature.[8]

Lanthanide–Polymer Complexes. The lanthanide salts of these polymers were prepared as follows.

Sodium acetate or ammonium hydroxide was added to the solution of polymer–$EuCl_3$. The resulting precipitate and solution were further stirred for 1 h. The precipitate was filtered, washed with water and methanol, and dried under vacuum at 60 °C for at least 1 day.

The salts of polymers with Eu/Tb, Tb/Co, and Tb/Co/Cs were prepared by adding the methanol–butanone solution of these weighed metal halides into the butanone solution of the polymers. Sodium acetate was added to precipitate the salts, which were purified as described above.

After the polymer was burned, the ash was tested for chloride with $AgNO_3$. No chloride was detected. A trace amount of Na in the salts was detected by atomic absorption measurements.

Polymer–$Eu(OAc)_3$ Blends. Polystyrene (Dow Chemical Co., MW = 30 000) was purified by reprecipitating from butanone into methanol. A mixture of polystyrene and $Eu(OAc)_3$–butanone solution was stirred overnight. After the solvent was removed, the solid obtained was ground to a fine powder and dried under vacuum at 60 °C for 2 days.

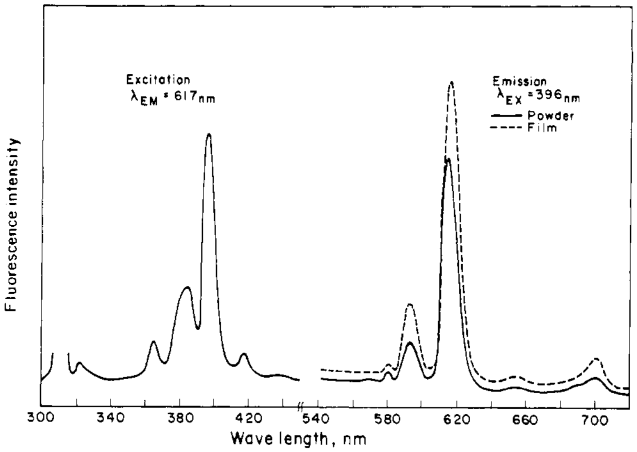

Figure 1. Excitation and emission spectra of PSAA-Eu^{3+} salt.

The weighed PMMA (Polysciences Inc., medium molecular weight) and $Eu(OAc)_3$ were dissolved in acetone and stirred overnight. After the solvent was removed, the material was dried as described above.

Determination of Metal Contents. Ashing Method. A polymer sample was weighed in a Pt or porcelain crucible and placed in a furnace. The temperature was raised to 600 °C at the rate of 200 °C/h and maintained at 600 °C for 1 h. The metal oxide residue was weighed and the metal ion content was calculated on the basis of the M_2O_3 stoichiometry. The identity of the lanthanide oxide was confirmed by X-ray powder diffraction.

Atomic Absorption Method. Europium, terbium, cesium, and cobalt contents were determined by an atomic absorption method. The metal oxide residue in the polymer ash was dissolved in a small amount of dilute HCl by heating and then diluted to the appropriate ranges of concentration of the elements.

A Model 303 Perkin-Elmer atomic absorption spectrophotometer was used for this purpose.

Fluorescence Measurements. A Model MPF 2A Hitachi Perkin-Elmer fluorescence spectrophotometer was used to measure fluorescence spectra of lanthanide-containing polymers. Powder samples were placed in the solid sample holder attached to the instrument, which measures the fluorescence at 90° to the exciting beam. The measurements were carried out at room temperature just after removing samples from a drying oven in order to avoid the quenching of fluorescence by adsorbed moisture. The nonuniformity of size and shape of powder samples may affect the fluorescence intensity. Thus, the powder sample was ground as fine and uniform as possible and kept dry until the measurements were taken. The sample was compressed well against the quartz window of the powder sample holder. The experimental error on fluorescence intensity was usually less than 5%.

Discussion and Results

The excitation and emission spectra of film and powder samples for PSAA–Eu complex were found to be identical, as shown in Figure 1. The bright red emission lines of Eu^{3+} at ca. 600 nm were assigned to transition from the $^5D_2$ levels to all the multiplet levels of ^7F. This emission spectrum was obtained under excitation at 396 nm, corresponding to the $^5L_7$ level of the Eu^{3+} ion. Similar fluorescence spectra of the PSAA–Tb complex were obtained as shown in Figure 2. The excitation spectrum for the Tb complex is broad compared with that of the Eu complex and the maximum is located at 305 nm. The relationship between fluorescence intensity and Eu or Tb content of PSAA complexes is shown in Figure 3. The intensity increases with increasing lanthanide ion content, reaches a maximum at 4–6 wt % of ions, and then decreases with further increase of ion content. The same tendency was also found in PMM/MA–Eu complexes

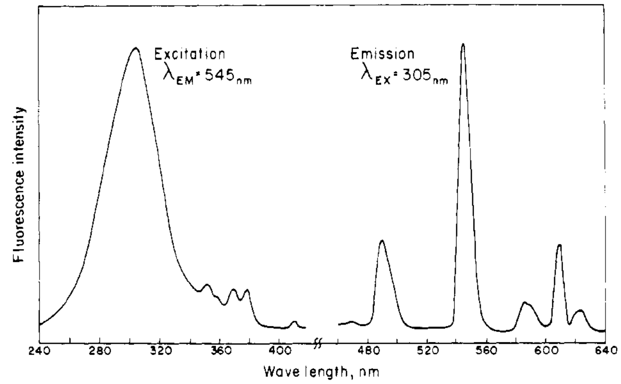

Figure 2. Excitation and emission spectra of PSAA-Tb^{3+} salt.

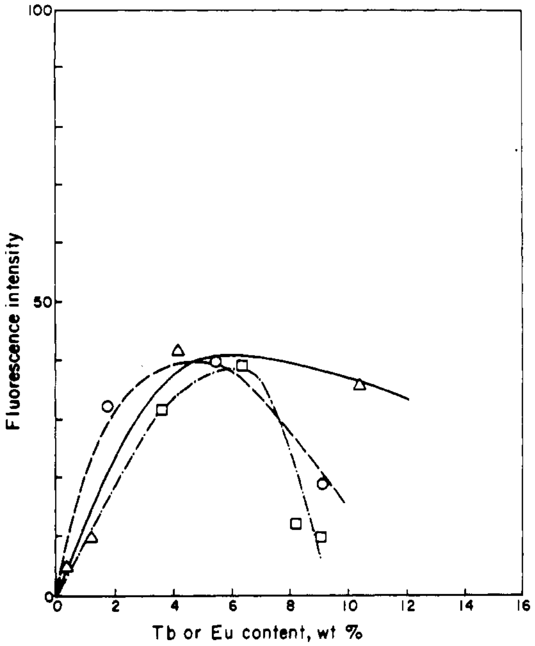

Figure 3. Relationship between fluorescence intensity and metal content: (○) PSAA (13 mol %)-Eu^{3+} salt; (△) PSAA (9 mol %)-Eu^{3+} salt; (□) PSAA (13 mol %)-Tb^{3+} salt.

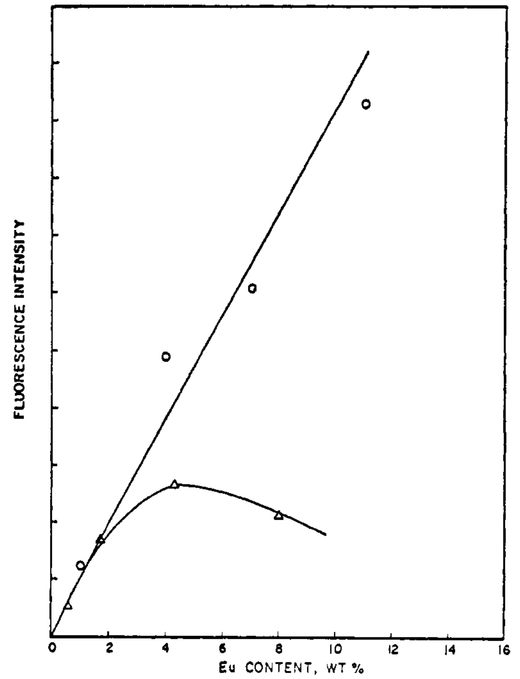

Figure 4. Relationship between fluorescence intensity and Eu^{3+} content in (○) PMMA-$Eu(OAc)_3$ and (△) PMM/MA-Eu^{3+}.

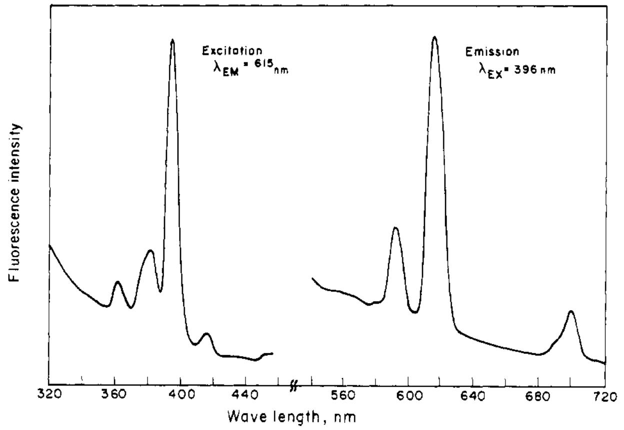

Figure 5. Fluorescence spectra of sulfonated polystyrene-Eu^{3+} salt.

(Figure 4). However, the lanthanide salts of poly(acrylic acid) and poly(styrene–maleic acid) show a linear increase of fluorescence intensity with increasing lanthanide ion content up to around 15 wt %. Linear relationships were also observed in samples in which $Eu(OAc)_3$ is uniformly dispersed in polymers such as polystyrene and poly(methyl methacrylate) (Figure 4).

The tendencies in the relationship between fluorescence intensity and lanthanide content of PSAA and PMM/MA complexes are typical of concentration quenching of fluorescence as described in the literature.[9] Deviation from linearity and concentration quenching clearly suggest formation of ionic aggregates in which metal ions are close together.

A study of the glass transition temperatures of ionomers suggests that both the charge and the size of the ion may affect clustering.[3] However, it is interesting to note that the concentration at which the maximum of the fluorescence intensity of PSAA–Eu complex (6 wt %; 4.0×10^{-4} mol/(g of salt)) occurs is in the same range of ion concentration where the aggregate formation started in poly(styrene–sodium methacrylate) ($\sim 5.7 \times 10^{-4}$ mol/(g of salt)).[10]

Recently Lundberg and Makowski[7] prepared partially sulfonated and carboxylated polystyrenes. They studied the differences of physical properties of these ionomers and found that the ionic association in the sulfonate is much stronger than in the carboxylate. Rigdahl and Eisenberg[11] investigated viscoelastic properties of sulfonated polystyrene. These results indicated that the time–temperature superposition for the Na sulfonate ionomer with low concentration (1.8 and 5.1 mol %) is valid. However, it breaks down for a sample containing 9.9 mol % salt. These results were accounted for by the increasing amount of clustered material at high concentration. In order to examine further the cluster structure in the styrene derivatives, we prepared Eu and Tb salts of the partially carboxylated and sulfonated polymers and measured their fluorescence spectra. Typical fluorescence spectra of these salts are shown in Figures 5 and 6. SPS–Eu has the same sharp excitation peak at 376 nm as PSAA–Eu and PMM/Ma–Eu complexes, which corresponds to the excitation of the Eu^{3+} ion itself. However, CPS–Eu shows broad peaks and different excitation maxima at shorter wavelengths (~371 nm). This indicated that an energy transfer from the ligand, i.e., the benzoate moiety to Eu^{3+}, occurred, as in Eu^{3+}–*o*-benzoyl benzoate.[12] However, in the case of the SPS–Eu complex no such energy transfer was observed.

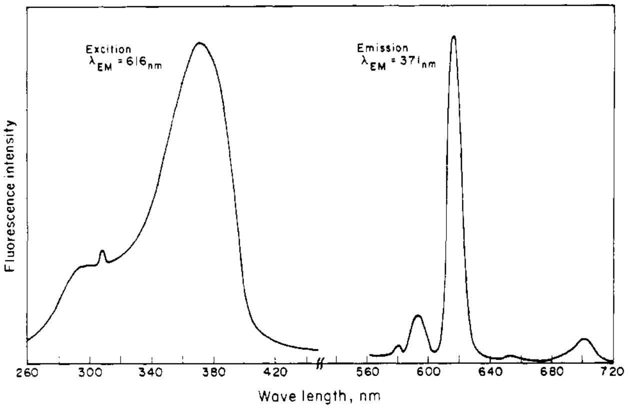

Figure 6. Fluorescence spectra of carboxylated polystyrene–Eu^{3+} salt.

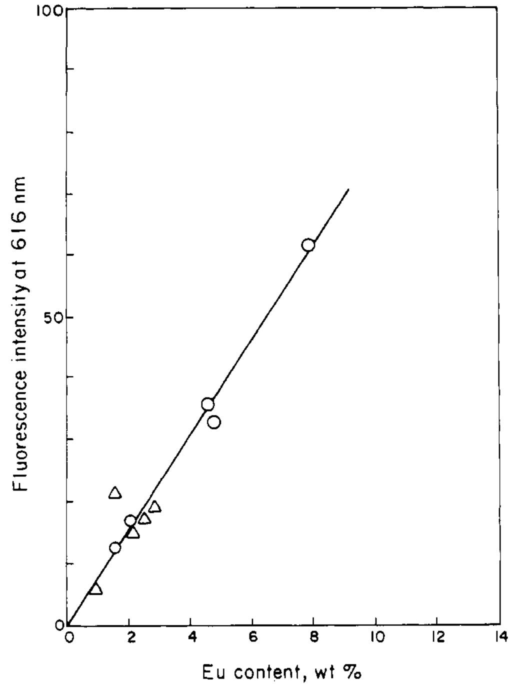

Figure 7. Fluorescence intensity vs. Eu content in sulfonated polystyrene–Eu^{3+} salt: (△) sulfonic acid content 2.6 mol %; (○) sulfonic acid content 6.1 mol %.

Typical relationships between fluorescence intensity and Eu or Tb content in SPS and CPS are shown in Figures 7 and 8. The fluorescence intensity of the SPS–ion complex increased linearly with increasing ion content. In the case of the CPS, the intensity also increased with the ion content and did not show the strong concentration quenching observed in PSAA- and PMM/MA-ion complexes. The results suggest that lanthanide ions in the SPS and CPS systems are homogeneously dispersed throughout the polymer matrix. On the basis of these measurements, it is concluded that partially carboxylated and sulfonated polystyrene ionomers do not contain ion aggregates up to 6 mol % ion.

Considerable effort has been devoted to the study of nonradiative energy transfer between fluorescent lanthanide donor–acceptor pairs in the solid state, particularly in glasses.[13-17] When the emission spectrum of the donor overlaps the absorption spectrum of the acceptor, excitation energy absorbed by the donor can be transferred to the acceptor over considerable distances. Thus, lanthanide ions were applied as fluorescent probes in the study on the conformations of biological molecules.[18] The metal ions which are native to metalloenzymes; e.g., Ca^{2+}, Mg^{2+}, and Zn^{2+}, are spectroscopically inactive. The substitution of trivalent lanthanides for these ions has been utilized in the elucidation of metal binding sites. Moreover, if some ions which act as donor or acceptor against the lanthanide ions are introduced, the distance between the metal binding sites may be estimated by measurements of energy transfer efficiency.

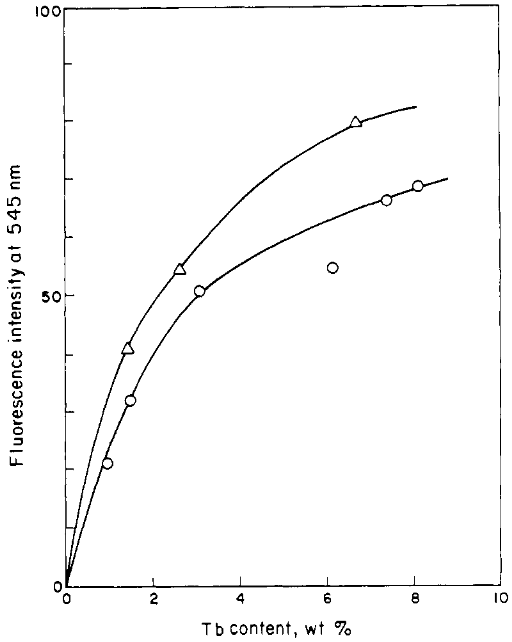

Figure 8. Fluorescence intensity vs. Tb content in carboxylated polystyrene–Tb^{3+} salt: (○) carboxylic acid content 5.0 mol %; (△) carboxylic acid content 6.4 mol %.

In analogy to the use of energy transfer between two metal ions as a "spectroscopic ruler" in biological systems, we attempted to elucidate the structures of various ionomers by using Tb–Eu and Tb–Co metal probes. Thus, Tb–Eu and Tb–Co metal ions containing poly(styrene–acrylic acid) and partially carboxylated and sulfonated styrenes were prepared and the energy transfers from Tb^{3+} to Co^{2+} and Eu^{3+} were measured by the Tb^{3+} fluorescence quenching behavior.

The relationship between fluorescence intensity of Tb^{3+} at 545 nm and Eu^{3+} content in PSAA–Tb/Eu salts is shown in Figure 9. At an equimolar content of Eu and Tb ions, the fluorescence of Tb was found to be quenched more than 90%. When the Tb^{3+} and Co^{2+} ions in the PSAA system were used as a probe, very efficient quenching of the Tb fluorescence was observed, as shown in Figure 10. Rather surprisingly the quenching effectiveness was sharply increased when spectroscopically inactive Cs ion was added to this system (Figure 10). These results indicate that Tb^{3+} and Co^{2+} ions are located very closely to each other and further confirm the existence of ion aggregates in the PSAA system.

Förster[19] and other investigators[20] using different approaches have arrived at the same formula for the probability $P_{D\rightarrow A}$ of dipole–dipole transfer between donors and acceptors which are statistically distributed. They show that in a viscous medium

$$P_{D\rightarrow A} = 2x \exp(x^2) \int_x^{\infty} \exp(-t^2)\, dt = \pi^{1/2} x \exp(x^2)[1 - \operatorname{erf}(x)] \quad (1)$$

where erf (x) is the error function. Here $x = C/C_0$ with

$$C_0 = \frac{3000}{2\pi^{3/2} N R_0^{\,3}} = \left(\frac{7.66 \times 10^{-8}}{R_0}\right)^3 \quad (2)$$

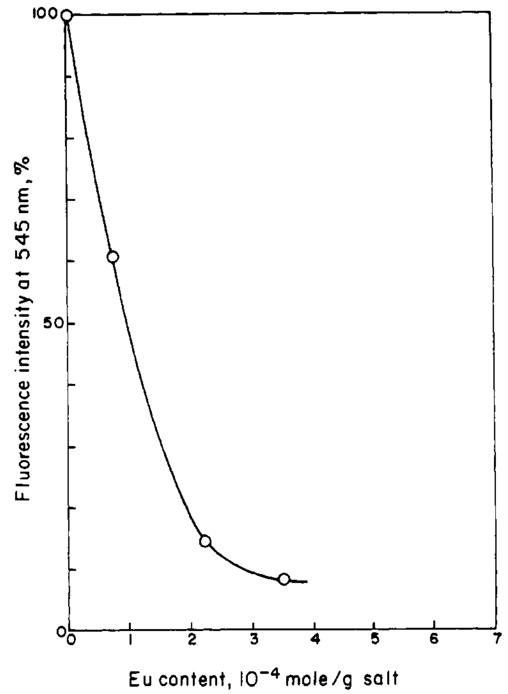

Figure 9. Energy transfer from Tb^{3+} to Eu^{3+} in poly(styrene–acrylic acid)–lanthanide salts.

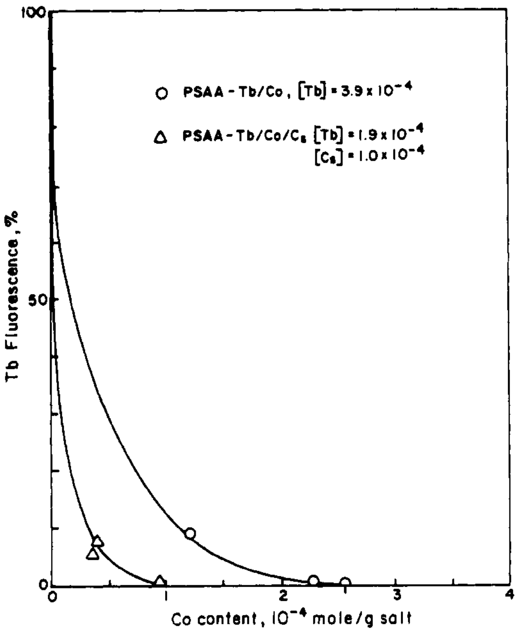

Figure 10. Energy transfer from Tb^{3+} to Co^{2+} in poly(styrene–acrylic acid)–lanthanide salts.

and C the concentration of the acceptor. The quantity C_0 may be regarded as a critical transfer concentration corresponding to a transfer efficiency of 76%. R_0 is the critical distance for 50% energy transfer given by

$$R_0^6 = 8.78 \times 10^{-25}\kappa^2 Q n^{-4} J \text{ cm}^6 \qquad (3)$$

where κ is the dipole–dipole orientation factor, Q is the donor quantum yield in the absence of energy transfer, n is the refractive index of the intervening medium, and J is the spectral overlap integral

$$J = \int_0^\infty F(\nu)\epsilon(\nu)\nu^{-4}\,d\nu \qquad (4)$$

where $F(\nu)$ is the spectral distribution of the donor emission normalized to unity, $\epsilon(\nu)$ is the molar extinction coefficient of the acceptor in units of cm^{-1} M^{-1}, and ν is the frequency in cm^{-1}.

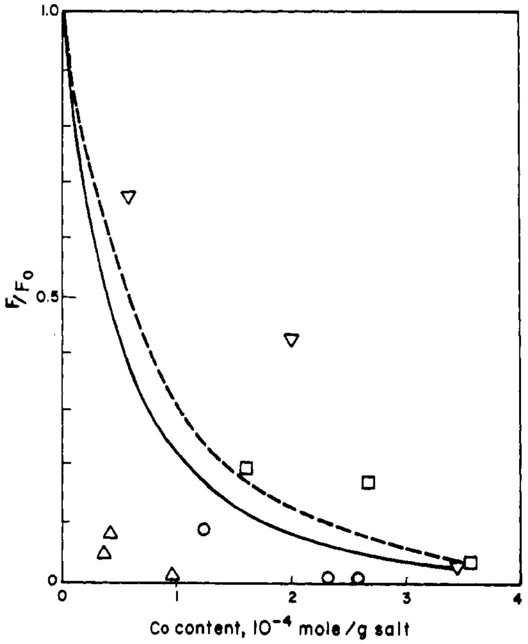

Figure 11. Relationship between relative fluorescence yield F/F_0 and Co concentration: (—) calculated F/F_0 value, R_0 = 17.3 Å; (---) calculated F/F_0 value, R_0 = 16.2 Å; (○) PSAA-Tb/Co, [Tb] = 3.9 × 10^{-4} mol/(g of salt); (△) PSAA-Tb/Co/Cs, [Tb] = 1.9 × 10^{-4}, [Cs] = 1.0 × 10^{-4} mol/(g of salt); (□) CPS-Tb/Co, [Tb] = 1.7 × 10^{-4} mol/(g of salt); (▽) SPS-Tb/Co, [Tb] = 1.4 × 10^{-4} mol/(g of salt).

The energy transfer probability is related to the relative fluorescence yield in the presence and absence of acceptor, F/F_0, by

$$P_{D\rightarrow A} = 1 - F/F_0$$

Thus, energy transfer occurs preferentially between close-lying donor–acceptor pairs.

In order to interpret the fluorescence quenching behavior of Tb^{3+} for ionomers containing Tb^{3+} and Co^{2+} ions, we calculated, using eq 3, the critical distance R_0 for our donor–acceptor pairs. The refractive index for polystyrene (n^{25}_D = 1.60) was used as a first approximation[21] because the degrees of carboxylation and sulfonation of the polystyrene were small (in the range of 4–5 mol %). The donor quantum yield Q = 0.51 and the spectral overlap integral J = 5.92 × 10^{-16} M^{-1} cm^3 for Tb–Co were taken from the literature,[18] yielding a critical distance R_0 = 17.3 Å, assuming $\kappa^2 = {}^2/_3$. The value C_0 was obtained by using R_0 = 17.3 Å from eq 2. The calculated F/F_0 values are plotted as a function of C in Figure 11.

In this figure, the fluorescence quenching behavior of Tb^{3+} obtained experimentally for PSAA–Tb/Co, CPS–Tb/Co, and SPS–Tb/Co were also plotted. The fluorescence quenching data for the PSAA system was found to be below the theoretical quenching curve. However, for CPS and SPS systems, the values of the quenching efficiency lay on or above the calculated curve.

The R_0 used for the calculation of theoretical quenching curve was obtained using a number of assumptions, i.e., the refractive index of pure polystyrene and the quantum yield Q for the $^5D_4$ level of Tb^{3+} bound to thermolysin.[18] If the refractive indexes for the ionomer systems were higher than that of polystyrene and the quantum yield was lower, the R_0 value would decrease and the theoretical quenching curve would move upward (see Figure 11).

Without further study, it is difficult to discuss these data quantitatively. However, these results indicated further that for the PSAA system, the metal ions were located closer to each other than for a statistical distribution of metal–metal distances and the metal ions in the CPS and SPS systems have longer metal–metal distances. This shows further that the CPS and SPS do not form ion aggregates or clusters.

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References and Notes

(1) (a) Abstracted in part from a dissertation to be submitted by Y. Ueba to the Polytechnic Institute of New York in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Polymer Science and Engineering (1980). (b) IREX exchange scholar from the USSR.
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Supermolecular Structure and Thermodynamic Properties of Linear and Branched Polyethylenes under Rapid Crystallization Conditions

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ABSTRACT: The crystalline morphology, or supermolecular structure, of polyethylenes crystallized under controlled nonisothermal conditions has been studied by light-scattering techniques. The morphological forms observed can be systematically changed with molecular weight and quenching temperatures and merge in a continuous manner with those previously reported for isothermal crystallization conditions. It is now possible to develop a random lamella-type morphology at much lower molecular weights than heretofore. Moreover, as a consequence of these studies, a variety of superstructures can be developed for the same molecular weight at the same level of crystallinity. Thus the different factors contributing to the properties of semicrystalline polymers can be separated and treated as independent variables. The influence on the morphology of different constitutional factors such as molecular weight, concentration of branch groups, and copolymer concentration is described. The thermodynamic properties of these systems are studied in detail, and it is found that there is no influence of the morphology (as an independent variable) on these properties.

Introduction

A lamellar crystallite, with its associated amorphous and interfacial regions, represents the elementary structural entity of a homopolymer crystallized from the melt.[1-4] These primary crystallites can, under certain circumstances, be organized into higher levels of crystalline morphology, or supermolecular structure. The commonly observed spherulitic structures are in this category. Detailed studies of linear polyethylene fractions[5-8] have shown that in fact a variety of crystalline morphological forms can be obtained. These develop in a systematic manner as the molecular weight and crystallization temperatures are varied. The main work that has been reported so far[8] covered a molecular weight range from about 1×10^4 to 8×10^6, the complete isothermal crystallization range, as well as one rapid (quenched) crystallization procedure. The most perfectly developed spherulites, essentially of the classical type, are observed in the lower molecular weight samples, $M \lesssim 8.5 \times 10^5$. In contrast, the higher molecular weight samples do not display any well-defined morphology under any crystallization conditions. The lower molecular weight, isothermally crystallized samples developed either a poorer spherulitic organization or rodlike forms, depending on the molecular weight and crystallization temperature. The crystalline morphology has been found to be extremely sensitive to molecular weight polydispersity.[7-9]

In contrast to the results for linear polyethylene, an initial study of low-density (branched) polyethylene samples showed that, for unfractionated polymers which were crystallized isothermally at low undercoolings and then cooled to room temperature, spherulitic structures always developed.[10] However, when these samples were quenched from the melt, a variety of morphological forms were observed which depended on the branching concentration and proportion of high molecular weight species present. The most highly branched sampled did not display any well-defined crystalline morphology.[10] However, branched