0.97 (s), 0.8–2.5 (m), 4.48 (m); ir (liquid film) 1012, 949 cm^{-1}. Anal. Found: C, 78.05; H, 11.84.

***trans*-2-*tert*-Butyl-*trans*-4-hydroxycyclohexanol (2).** The above diol was isolated from an isomeric mixture of the hydrogenation product by preparative gas chromatography using a 3.0 m × 3 mm column packed with carbowax 6000 on 60/80 celite at 178 °C with hydrogen gas (1.0 kg/cm^2). Crude diol obtained was recrystallized from acetone to yield a product with mp 174–175 °C (sealed tube). The structure of 2 has been established by the following results. The melting point is different from the melting points of the two known isomers, i.e., *cis*-2-*tert*-butyl-*cis*-4-hydroxycyclohexanol,[17] mp 152.5–153.5 °C, and *trans*-2-*tert*-butyl-*cis*-4-hydroxycyclohexanol,[13] mp 156.5–157.7 °C. The NMR spectrum of the diacetylated sample of 2 in CCl_4 showed a broad peak due to two methyne hydrogens at C-1 and C-4. It is generally known that the NMR peak of the axial methyne hydrogen is broad, whereas that of the equatorial one is sharp.[13,14] Thus, the two methyne hydrogens of 2 are reasonably assumed to be at the axial positions. The elemental analysis of 2 is in agreement with the calculated values. Found: C, 70.01; H, 11.84. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Its NMR spectrum is shown in Figure 1b.

Polymerization Procedure. BF_3–THF complex (catalyst), ECH (promotor), and CH_2Cl_2 (solvent) were purified as previously described.[6–8] Polymerization was carried out under dry nitrogen and stopped by the addition of Na phenoxide in THF. The polymer solution in CH_2Cl_2 was washed with aqueous NaOH, dried over anhydrous K_2CO_3, and finally evaporated to dryness in vacuo. Further purification of the polymer was performed by methanol (solvent)–water (precipitant) reprecipitation.

Hydroboration of Poly 1d. To 90 mg of poly 1d in diglyme (2 ml) was added $NaBH_4$ (15 mg) at 0 °C and then BF_3–etherate (0.03 ml) after stirring for 2 hr. The suspension was kept overnight at room temperature and refluxed in propionic acid (1 ml) for 4 h. The reaction mixture was diluted with water, extracted with ether, and washed with aqueous $NaHCO_3$. The ether solution was evaporated to dryness in vacuo.

Measurement of NMR and Ir. Nuclear magnetic resonance spectra were determined in $CDCl_3$ or CD_3OD on a PS-100 or C-60H (Jeol Ltd.) at room temperature. Infrared spectra were recorded on a DS-301 spectrometer (Nihon Bunko Co., Ltd) as film coated on a NaCl plate.

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Kinetics of Delayed Luminescence and Triplet Energy Migration in Poly(*N*-vinylcarbazole)

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ABSTRACT: The kinetics of phosphorescence and delayed fluorescence of solid films of poly(*N*-vinylcarbazole) have been examined over a temperature range from −150 to −75 °C. Delayed fluorescence intensities (I_{df}) go through a maximum at −100 °C, but phosphorescence intensities (I_p) decrease monotonically with increasing temperature. At −100 °C and with sufficiently low light intensities I_{df} and I_p are biphotonic and monophotonic, respectively. Both luminescence intensities decay exponentially at −100 °C and the lifetimes show an approximate factor of 2 ratio as expected for annihilation delayed fluorescence. A better explanation for the lifetime data is provided if one assumes that the delayed fluorescence arises from an annihilation process involving a mobile triplet and an immobile triplet excimer. In any case, it appears that triplet migration is intermolecular in character.

Triplet energy migration in polymers has been studied by a number of techniques involving phosphorescence or delayed fluorescence measurements.[1–8] Most of the earlier work was carried out on frozen solutions, but more recently, solid polymer films have been studied as well. Of special interest in the present work is the study of Cozzens and Fox,[5] who demonstrated that frozen solutions of poly(1-vinylnaphthalene) display an intramolecular type of triplet energy transfer judging from the kinetics of the delayed fluorescence emission and the behavior of triplet quenchers.

Because of our recent interest in the mobility of triplets in liquid solutions of monomeric species, as measured by spatially nonhomogeneous irradiation,[9] it was decided to study the kinetics of polymer delayed luminescence to see if conditions could be found such that this same experimental technique could be applied to polymer systems. The major question to be settled was whether or not annihilation (or P type) delayed fluorescence ever occurs by a mechanism involving intermolecular triplet migration. The question is important since the technique of spatially intermittent radiation cannot be applied when the triplet–triplet processes are intramolecular in character. Obviously, dilute frozen solutions are a poor choice for study and so it was decided to examine the kinetics of phosphorescence and delayed fluorescence of solid polymer films.

At the commencement of this work, no published reports of delayed fluorescence from a solid polymer film could be found. In recent months, however, Fox and co-workers[7] have reported on studies of delayed fluorescence from solid films of poly(vinylnaphthalene) and its copolymers with methyl methacrylate and with 2-naphthyl methacrylate as

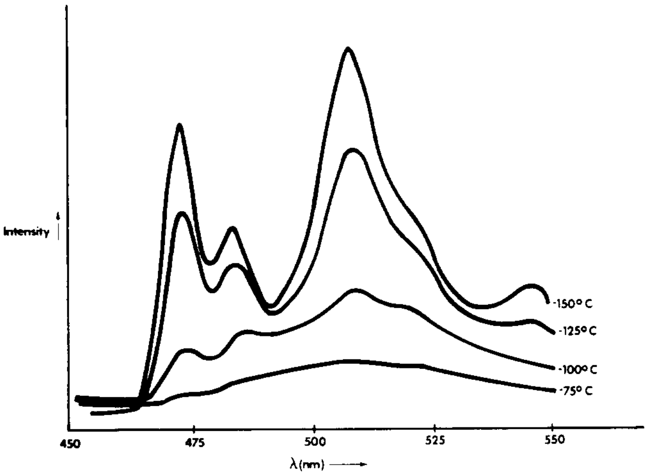

Figure 1. Phosphorescence of a solid PVCA film using Xe lamp excitation at various temperatures.

well as poly(2-naphthyl methacrylate) itself. In addition, Avakian and co-workers[10] have mentioned observing delayed fluorescence from several polymer films including poly(*N*-vinylcarbazole) (PVCA) and Klöpffer[11] has observed the PVCA delayed fluorescence as well.

In the present work, an attempt has been made to elucidate the mechanism of triplet migration in films of PVCA by a detailed study of the kinetics of the phosphorescence and delayed fluorescence. To accomplish this, experiments have been carried out on the temperature dependence of the delayed emission and, in addition, extensive use has been made of computer methods to examine critically the degree to which the luminescence decays obey an exponential law and to evaluate luminescence lifetimes.

Experimental Section

The phosphorimeter used in these experiments was constructed in the laboratory. The excitation source was a 250-W xenon lamp the emission from which was filtered with an OX7 filter transmitting between 250 and 430 nm. Excitation and emission beams were chopped using slotted disks rotating on a common axle but with slots arranged so that emission and excitation were 180° out of phase. Rotation speeds could be varied from a few rpm to 10 000 rpm using a variable speed control unit (Servomex Controls Ltd. controller type MC47). The emission was focussed onto the slits of a monochromator (Hilger and Watts Model D330) having a reciprocal dispersion of 26 Å/mm. In all experiments the slit setting was 2 mm or less.

Detection of the emission signal was accomplished using an EMI 9789 photomultiplier with the 100 kohm resistors wired in a linear array. When spectra were being recorded the photomultiplier output was sent to a DC amplifier and then to an X–Y recorder (Hewlett-Packard Model 7035B). The photomultiplier dynode voltage was provided by a Brandenburg Model 476R, constant voltage source.

When measuring luminescence lifetimes, the photomultiplier signal was sent to a Northern Scientific Model NS-600 signal averaging instrument. A light emitting diode and detector was mounted on the excitation chopper and positioned to yield an electrical signal in synchronization with the beginning of each luminescence decay event. The rise time of this signal was not fast enough to initiate a signal averaging sweep and so it was first sent to a Schmidt trigger which, in turn, triggered the signal averager.

The rising edge of the emission signal required about 40 ms under the usual measurement conditions. Since the luminescence lifetimes typically varied between 200 ms and several seconds, no deconvolution of the emission signal was used and all computed quantities utilized data from the tail of the decay. The data from a given lifetime measurement were stored on teletype sheets and punched tape. Lifetimes were determined by least squares computer fits to a single exponential. The relative background or stray light signal could be calculated directly with this program. Even with the weakest signals it was found to be less than 5% and usually about 0.9%.[12]

Most of this work was carried out using Luvican M170 poly(vinylcarbazole) (PVCA) obtained from Dr. W. Klöpffer. It has a viscosity average molecular weight of 9×10^5. The polymers were purified by repeated cycles of dissolution in toluene followed by reprecipitation in methanol. During the course of this work it was found that useable delayed fluorescence signals could be obtained only from thoroughly degassed samples. These were prepared by placing a toluene solution of the polymer in a 6-mm quartz tube joined via a graded seal to a standard taper joint which could be connected to a vacuum system. After degassing to 1.5×10^{-5} Torr, the toluene was slowly evaporated into an adjacent cold trap while the solution in the tube was rotated to assure a somewhat uniform coating of the polymer on the tube walls. After the evaporation was completed, vacuum pumping was continued for about another half hour to remove the final traces of solvent. When this was accomplished the sample was sealed off using a hand torch.

The sample was mounted in a variable temperature cryostat cell holder which could be conveniently operated at controlled temperatures from −150 to 50 °C (manufactured by Research and Industrial Instruments Co., London, S.E. 26).

A series of neutral density filters was also prepared for use in attenuating the excitation beam by precisely known amounts. They consisted of thin films of carbon black sandwiched between two quartz plates. Optical absorption measurements showed that the transmittances of these plates varied by less than 5% between 300 and 400 nm, a wavelength range which includes the PVCA absorption band. The fractional amount of excitation light transmitted by these filters was determined by a direct measurement of the relative excitation intensities using the same optical system as was used for the delayed luminescence work, but with the choppers rotating in phase.

The solvents used were spectroscopic grade materials, the methanol from Hopkins and Williams Ltd., and the toluene from Eastman Kodak Co.

Results

In Figure 1, phosphorescence spectra of a degassed sample of the purified Luvican M170 polymer are shown at 25° intervals from −150 to −75 °C. Two major emission signals appear at about 505 and 475 nm. The PVCA film spectra previously reported by Klöpffer[1] also show two signals, one slightly below and one above 500 nm, but with lower resolution and somewhat different relative intensities. Identical spectra to those shown here were obtained using films prepared on quartz disks by solvent evaporation in the air. That is, degassing did not change the appearance of the phosphorescence spectra. A PVCA sample obtained from Cellomer Associates yielded a phosphorescence spectrum essentially identical with that reported by Klöpffer. All of the phosphorescence spectra showed the same monotonic decrease of emission intensity with increasing temperature as is demonstrated in Figure 1.

In Figures 2 and 3 are shown spectra of a delayed luminescence from the purified and degassed Luvican M170 PVCA which is believed to be delayed excimer and monomer fluorescence. The resolution here is very poor and both polymer samples yielded similar emission spectra in this wavelength region. Unlike the phosphorescence, the delayed fluorescence intensity exhibits a maximum at about −100 °C. Thus, with regard to temperature dependence, the delayed fluorescence of these PVCA films is similar to that observed for liquid solutions of pyrene.[13] A barely detectable delayed fluorescence signal could be observed in nondegassed films, but was too weak to be useable.

It should be mentioned that many attempts to observe delayed fluorescence in PVCA films were made on samples which had been dissolved in chloroform and reprecipitated with methanol. No delayed fluorescence was observed in any of these experiments. Presumably the last traces of chloroform are difficult to remove, perhaps due to an acid–base interaction between the chloroform proton and the PVCA nitrogen. In any event, residual chlorine atoms

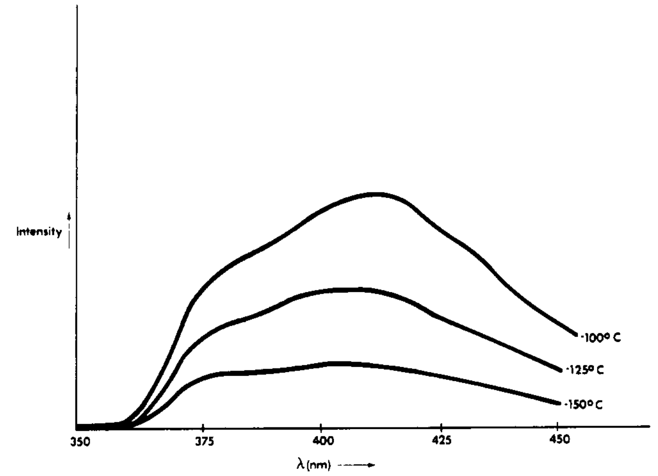

Figure 2. Delayed fluorescence of a solid PVCA film at −150, −125, and −100 °C using Xe lamp excitation.

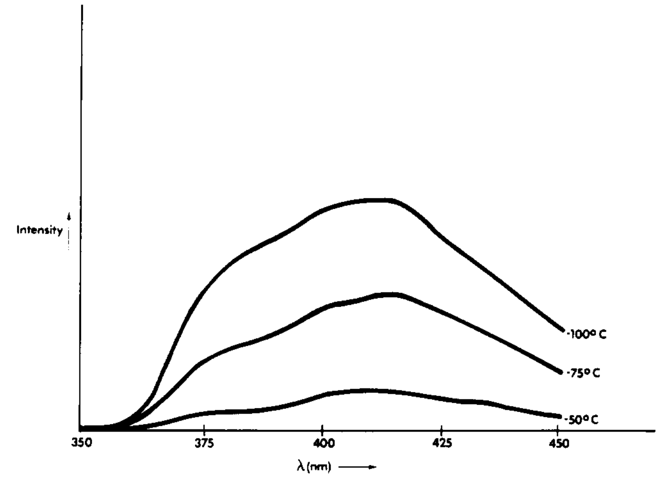

Figure 3. Delayed fluorescence of a solid PVCA film at −100, −75, and −50 °C using Xe lamp excitation.

present would give rise to enhanced triplet quenching and a greatly diminished probability of delayed fluorescence.

Several series of experiments were carried out to determine how the emission intensity depends upon the magnitude of the excitation intensity. The three neutral density filters were inserted, one at a time, into the excitation beam and, from relative values of the emission signals observed, n was calculated from the equation

$$(I_x/I_{x0})^n = I_m/I_{m0}$$

where I_x and I_m represent intensities of excitation and emission, respectively, and the subscript zero indicates conditions in which the excitation light was unattenuated. Experiments of this type were carried out using two different ranges of the excitation intensity the lower of which was achieved by altering the optical system so that the focal point occurred a few centimeters beyond the sample. An effective reduction in light intensity of approximately 0.4 was achieved using this defocussed beam. In Table I are found values of n for delayed fluorescence ($n(410)$) and n for phosphorescence ($n(505)$) obtained using this lower range of light intensities.

Table I
Values of n Showing the Dependence of the Phosphorescence and Delayed Fluorescence on the Intensity of the Excitation at −100 °C[a]

I_x/I_{x0}	n delayed fluorescence 410 nm	n phosphorescence 505 nm
0.661	2.0	1.0
0.558	2.1	1.0
0.320	2.1	1.1

[a] These are averages of four measurements.

It is quite clear that the emission at 410 nm is biphotonic in character and probably results from annihilation delayed fluorescence. It should be noted that, at higher incident light intensities, values of $n(410)$ as low as 1.7 and values of $n(505)$ of 0.76 were observed. Thus, it is apparent that, at sufficiently high light intensities, second-order processes for the removal of triplets compete effectively with first-order processes.

In frozen polymer solutions biphotonic kinetics are observed, even for strictly intramolecular triplet migration, because of multiphotonic absorption on single polymer molecules.[5] This leads to the creation of an array of essentially distinct chemical species containing one, two, or more electronically excited chromophoric groups each with its own characteristic mode of decay kinetics and associated lifetime. If processes leading to phosphorescence and delayed fluorescence involve independent pathways and arise from chemically distinct species, then there is no necessary factor 2 relation between the lifetimes of these two types of luminescence. For solid polymer films, chain entanglement is presumably extensive enough to permit intermolecular transfer of electronic excitation to occur to a certain extent. This would then provide a means whereby coupling between phosphorescence and delayed fluorescence processes could take place so that each process would depend, for its intensity, on the same pool of triplet species. If this were the case, and if biphotonic delayed fluorescence is observed, then both types of delayed luminescence should show exponential behavior and there should be a factor of 2 relation between the respective lifetimes.

Using these ideas, experiments were carried out to test PVCA films for the existence of intermolecular triplet transfer. Both phosphorescence (505 nm) and delayed fluorescence (410 nm) decays were recorded on the 512 channels of the signal averager and were stored on paper tape. The data were then tested for a fit to the equation

$$I = S + I_0 \exp(-t/\tau)$$

where S represents the intensity of scattered light, I_0 and I are luminescence intensities at times zero and at subsequent times, respectively, and τ is the lifetime of the luminescence. The best fit parameters were those which yielded a minimum value of χ^2 calculated using the standard statistical formulations. Computed values of χ^2 and the best-fit lifetimes are recorded in Table II. In each measurement only 320 of the 512 available data channels were used.

The statistical χ^2 values indicate a probability, well in excess of 99%, that both luminescence decays are indeed exponential. In both sets of measurements there is perhaps a suggestion that the lifetimes increase with decreasing excitation intensity, but it is probably preferable to treat the data homogeneously. Thus, the average phosphorescence lifetime is 574 ± 45 ms and the average delayed fluorescence lifetime is 258 ± 12 ms. The ratio between these two

Table II
Lifetimes and χ^2 Values Indicating Degree to Which Luminescence Decays are Exponential for Phosphorescence (505 nm) and Delayed Fluorescence (410 nm) of PVCA Films at −100 °C

Emission wavelength, nm	Rel excitation int	χ^2	τ, ms
505	1.0	1.30	487
505	0.32	1.32	601
505	0.25	1.13	595
505	0.08	1.85	611
410	1.0	2.26	259
410	0.32	1.30	235
410	0.25	2.95	257
410	0.08	1.05	281

lifetimes is 2.2 ± 0.27. Thus, within experimental error it may be said that the factor of 2 relationship between phosphorescence and delayed fluorescence lifetimes is observed here.

In addition to these measurements made on the major luminescence signals, similar data were obtained for the phosphorescence signal at 475 nm. Again, the decay is found to be exponential with an average lifetime of 475 ms.

Discussion

The results of Table II provide a good argument in favor of intermolecular migration of triplet excitation. The choice of temperature for these experiments proved to be quite important since at significantly lower temperatures than −100 °C it was not possible to achieve biphotonic kinetics while at higher temperatures the phosphorescence intensity becomes unmanageably small.

From the temperature dependence of the phosphorescence it is evident that the triplet quenching rate increases rapidly with rising temperature so that first-order processes for the removal of triplets compete more and more favorably with the second-order annihilation reactions. Nonexponential delayed fluorescence decays have been reported by Fox and co-workers[7] for several different polymers; however, these too might exhibit exponential behavior at appropriately selected temperatures.

The major phosphorescence emissions at 505 and 475 nm suggest the existence of at least two types of triplets. The lower energy species probably is associated with an immobile trap site but, because of the existence of annihilation delayed fluorescence, the higher energy triplet must be mobile. If we use $^3M^*$ to symbolize the mobile triplet species and $^3D^*$ to symbolize the trapped species then the mechanism would include:

$$^3M^* \rightarrow {}^3D^* \tag{1}$$

$$^3M^* \rightarrow {}^1M^0 \tag{2}$$

$$^3D^* \rightarrow {}^1M^0 \tag{3}$$

$$^3M^* + {}^3D^* \rightarrow {}^1D^* + {}^1M^0 \tag{4}$$

It is assumed that the rate of $^3M^*$ formation is proportional to the excitation intensity, that steps 2 and 3 include both radiationless and radiative processes, and that the rate of delayed fluorescence is equivalent to the rate of step 4. Application of steady state conditions to this mechanism leads to the result that phosphorescence should be purely monophotonic and delayed fluorescence purely biphotonic if step 4 is not involved in determining the steady state concentrations of $^3M^*$ and $^3D^*$. That is, it must be assumed that $k_3(k_1 + k_2) \gg k_4 I_a$ where I_a is the intensity of absorbed radiation.

According to step 4 of the mechanism, the lifetime of the delayed fluorescence should be related to the phosphorescence lifetimes associated with $^3M^*$ and $^3D^*$. These are 574 and 475 ms, respectively. Thus, $\tau_{df} = \tau(475)\tau(505)/[\tau(475) + \tau(505)]$ and the predicted value is then 260 ms which compares very favorably with the measured value of 258 ms. If the observed delayed fluorescence arose entirely from $^3M^*$–$^3M^*$ interactions the predicted lifetime would be 287 ms. Thus, the spectral properties of the luminescence and the relative lifetime measurements both agree better with a $^3M^*$–$^3D^*$ interaction as the source of the delayed fluorescence.

The temperature dependence of the phosphorescence and delayed fluorescence represents one of the most interesting features of these data and is found here to be very much the same as has been found earlier by Birks, Srinivasan, and McGlynn[13] in their study of pyrene in a viscous solvent. In this work it was pointed out that the rates of both intersystem crossing and excimer formation increase with increasing temperature and that this gives rise to a maximum in the quantum efficiency of triplet formation (ϕ_T). In the present case it still seems likely that the rate of excimer formation would increase with increasing temperatures, but it is not known if there is a triplet level in PVCA which can be thermally populated from S_1. Even if ϕ_T does exhibit a temperature maximum, however, radiationless processes associated with eq 2 and 3, due in part to impurity (oxygen) quenching, have a sufficiently large negative temperature dependence that the overall effect is a decrease in intensity with rising temperature.

The temperature maximum observed for the delayed fluorescence may arise in part from a maximum in ϕ_T but other processes must also make their contribution. For example, quantum yields of both molecular and excimer fluorescence generally have negative temperature coefficients whereas that for the radiationless deactivation of triplets to the ground state is positive. These three factors provide a qualitative explanation for the decrease of delayed fluorescence intensity with rising temperature.

Probably the primary cause of the decrease in delayed fluorescence intensity with falling temperatures below −100 °C is a decrease in the rate of step 4. The Arrhenius graph for these low-temperature data is linear and yields an activation energy of 1200 cal/mol or 420 cm^{-1}. Such a value is consistent with the triplet energy transfer occurring by way of accordion-like vibrational motion of the polymer chain, but with a sufficiently high frequency, however, that it is likely that the process would involve the cooperative motion of only a small number of chain segments.[14]

Thus, the data do provide support for the idea that, in solid films of PVCA, irradiation produces both mobile and trapped triplets and that intermolecular triplet migration occurs. It further indicates that the delayed fluorescence at 410 nm is annihilation delayed fluorescence resulting from the interaction of excimer and monomer triplets.

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Infrared Studies of Ionic Aggregation of Ethylene- and Butadiene-Based Ionomers

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ABSTRACT: An infrared spectroscopic investigation of the Na^+, K^+, Rb^+, and Cs^+ salts of ethylene– and butadiene–methacrylic acid copolymers has been carried out. The absorption due to the asymmetric stretching mode of the carboxylate ion contains two components: one at 1550 cm^{-1} and another at 1565 cm^{-1}. The ratio of peak intensities of these bands depends upon ion concentration, the nature of the cation, and temperature. It is concluded that the ion pairs in these copolymers are likely to exist in at least two types of ionic aggregates of different structures. Infrared dichroism studies established that the dichroic ratios of the 1550- and 1565-cm^{-1} bands depend on ion concentration in copolymers. The model systems, anhydrous salts of fatty acid, were also studied. A combination low-angle x-ray scattering and infrared data leads to a probable model of the ordered structure existing within ionic clusters.

During the past decade considerable attention has been paid to the investigation of physical properties of ion-containing polymers.[1-3] However, several major questions concerning the state of ion aggregation still remain open. Among many experimental techniques employed, infrared spectroscopy,[4,5] x-ray diffraction,[7-9,18] electron microscopy,[7,10] dynamic mechanical,[7,9,11] dielectric,[7,16] and nuclear magnetic resonance relaxation[16] tests should be cited. In spite of these efforts we still do not know whether the ions are dispersed on a molecular level as ion pairs or perhaps quartets, or more extensive clusters. One should add that structural features of ionic clusters are unknown.

In this paper an attempt is made to obtain additional evidence for ion clustering in ethylene- and butadiene-based ionomers using the ir technique. We studied the infrared bonds due to the stretching mode of carboxylate (COO^-) ions.

It is well known that the frequencies or infrared absorption bands are sensitive to the surrounding groups and therefore frequencies of absorption bonds assigned to the (COO^-) stretching mode can be employed for observation of the states of ionic aggregation. However, no conclusions can be drawn from the quoted studies of these ionomers[4,5] since only a broad featureless band due to the (COO^-) stretching vibration is observed. This picture can be explained by the presence of water and nonionized carboxylic groups which is known[18] to influence the degree of ion aggregation. Therefore it is necessary to investigate anhydrous and completely neutralized copolymers in order to observe the clusters with ordered structure.

Experimental Section

The starting material was a partially ionized copolymer of ethylene and methacrylic acid (trade mark "Surlyn"). The methacrylic acid content of the copolymers was 4.1 mol %. The starting material was refluxed in tetrahydrofuran with dilute hydrochloric acid in order to bring the copolymer in the nonionized state. This copolymer was further dissolved in hot xylene and films were cast from the solution. In order to obtain the Na^+, K^+, Rb^+, and Cs^+ salts of copolymers, ethoxides of sodium and potassium and hydroxides of rubidium and cesium were used for neutralization. The films were placed in a 95:5 mixture of xylene and ethanol with sodium or potassium ethoxides or with rubidium or cesium hydroxides at 20 °C for 20 min. After this treatment the ionized copolymers were washed with ethanol and dried in vacuo at 100 °C. The starting butadiene–methacrylic acid copolymers ("carboxylate rubber") contain 1.1, 2.4, and 4.9 mol % of methacrylic acid. These copolymers were dissolved in benzene and from this solution films were cast on a CaF_2 plate. In order to produce the ionized form these films were introduced in a 95:5 mixture of hexane and benzene with ethoxides of sodium or potassium or hydroxides of rubidium or cesium at 20 °C for 20 min. The subsequent procedures, such as washing and drying, were the same as those employed for the ethylene–methacrylic acid copolymers.

Infrared analysis indicated that the samples were 100% neutralized. The swelling agents used during neutralization favor the ion aggregation. Infrared spectra of the films were obtained on the UR-20; Perkin Elmer M 180, and FIS-3 Hitachi spectrophotometers. Temperature-dependent infrared studies were made using a special temperature cell. Temperature was measured using a calibrated copper–constantan thermocouple.

Results and Discussion

The infrared spectra of the three samples investigation are shown in Figure 1. It is obvious that both the 1740- and 1700-cm^{-1} –C=O stretching vibrations are absent. Instead of them two new peaks appear: one at 1530–1580 cm^{-1} interpreted as a (COO^-) asymmetric vibration and another at 1400–1420 cm^{-1} corresponding to a (COO^-) symmetric stretching vibration (Figure 3). It is seen from Figure 1 that the absorption due to the asymmetric stretching mode of the carboxylate (COO^-) ion consists of at least two compo-