Effects of Charge-Transfer Interactions in the CP-MAS ^{13}C NMR Spectra of Copolymers and Blends

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ABSTRACT: Polymeric charge-transfer complexes involving (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM) and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBEM) structural units are investigated by CP-MAS ^{13}C NMR spectroscopy. Models for the structural units (the acetates) show upfield shifts for most of the carbons involved in charge-transfer complexation. The shifts vary between 1 and 5 ppm. They are less obvious in the polymer spectra, due to a general broadening of signals induced by different types of polydispersity. Both model and polymer complexes (a blend of the two homopolymers and a copolymer) present single $T_{1\rho}$H values. There is a depression of these values in the complexes as compared with the additivity line, and this is discussed by analogy with the increase in the glass transition temperature due to complexation.

Introduction

Charge-transfer interactions play an important role in the supramolecular structure of many organized systems. One of the consequences of charge-transfer interaction can be modification of phase structure in some polymer blends. Electron-donor and electron-acceptor groups can be introduced onto immiscible polymer chains to improve compatibility.[1] Another consequence can be an increase in the glass transition temperature of a polymer or a blend that contains electron-donor and electron-acceptor groups. According to Kwei,[2] the expression for the T_g of a polymer blend where interactions occur contains a quadratic term qw_1w_2 in which w_i is the weight fraction of component i and q could be considered a measure of the efficacy of interactions. In a copolymer containing interacting groups, the deviation from the additivity line can be analyzed in terms of alternating diad fraction.[3] Still another consequence of charge-transfer interactions, and one of the main reasons to investigate complexes, is that their photoconductivity is directly related to the charge-transfer interactions.[4-6] To improve the photoconductivity, one has to design a polymer structure that would maximize interaction. These are just a few areas where charge-transfer interactions in polymers have been the subject of intense studies.

One of the methods to measure the strength of charge-transfer interactions in polymers is NMR spectroscopy. A change in electron density generated by the partial electron transfer from the donor to the acceptor will have as its main effect a chemical shift, upfield for the acceptor (higher electron density, more shielding) and downfield for the donor (lower electron density, less shielding). Probably the best example of such an observation is the solid-state high-resolution ^{13}C NMR spectrum of a complex of hexamethylbenzene (donor) with different acceptors.[7] Solution NMR spectra are also sensitive to charge-transfer interactions, and in a series of papers analyzing copolymer charge-transfer complexes, the upfield shift of the aromatic protons belonging to the electron acceptor structural unit was considered a measure of the charge-transfer interaction.[8] Carbon-13 chemical shifts are more sensitive to the electron density, so some of these copolymers were investigated by ^{13}C NMR spectroscopy in solution. Upfield shifts were observed for both donor and acceptor groups, and they were explained by the predominance of the aromatic shielding effect in stacked structures of aromatic donor and acceptor groups.[9] Solution spectra always reflect some influence of the solvent, and in copolymer charge-transfer complexes there are two competing phenomena: intra- and intermolecular interaction.[10] Blends of polymers containing donor groups with polymers containing acceptor groups eliminate any intramolecular interaction and can be considered a model for strongly interacting systems.[11] For this last series of studies, DSC was the method of choice that measured the overall interaction enthalpy, recognizing that some other kinds of interaction are certainly present in these systems.

Our studies are centered mainly on cross polarization magic angle spinning (CP-MAS) NMR spectroscopic investigation of polymer charge-transfer complexes. As described previously, one expects changes in chemical shifts resulting from different electronic density at the complexing sites. For a complex of poly(*N*-vinylcarbazole) (PNVC) with 2,4,7-trinitro-9-fluorenone (TNF), high upfield shifts of some TNF carbons could be observed.[12] With 2,4,5,7-tetranitro-9-fluorenone (TENF) as acceptor, the results were similar.[13] However, more interesting than the chemical shift analysis, values of the proton spin-lattice relaxation in the rotating frame ($T_{1\rho}$H) provide information on the spin diffusion in the complex, indirectly indicating proximity and molecular mixing. It is well-known that spin diffusion in a polymer blend will reflect its phase structure,[14,15] and some recent papers analyzed spin diffusion in different polymer blends.[16] In this paper, chemical shift changes and $T_{1\rho}$H values are measured for polymer charge-transfer complexes containing (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM) as donor structural unit and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBEM) as acceptor structural unit.

Experimental Section

NECMM and DNBEM were synthesized and polymerized by procedures described elsewhere.[10] Models for the two structural units were also synthesized according to described procedures.[10] They were (*N*-ethylcarbazol-3-yl)methyl acetate (NECMA) as the donor model and 2-[(3,5-dinitrobenzoyl)oxy]ethyl acetate (DNBEA) as the acceptor model. A 1:1 mole blend of poly(NECMM) and poly(DNBEM) was prepared by mixing the measured THF solutions of the two polymers (the orange color appears instantaneously upon mixing indicating complexation) and then precipitating the complex in a large quantity of a nonsolvent (methanol). The homopolymers are white, while the blend powder is orange. A 1:1 mole copolymer of NECMM with DNBEM was synthesized by radical copolymerization in toluene, following the procedure and the reactivity ratio values published elsewhere.[17] The copolymer was reprecipitated in methanol from a THF solution to provide an orange powder. Copolymer composition was verified by ^{1}H NMR spectroscopy in a CDCl$_3$-DMSO-d_6 mixture. Complexes of the models were prepared by using two procedures. In the first one, THF solutions of the two models were mixed in a 1:1 mole ratio, and the solvent was allowed to slowly evaporate. The solid complex was reddish-orange. The second procedure was designed to provide only a physical mixture, minimizing the charge-transfer interactions. The two powders were ground separately and then mixed in a 1:1 mole ratio.

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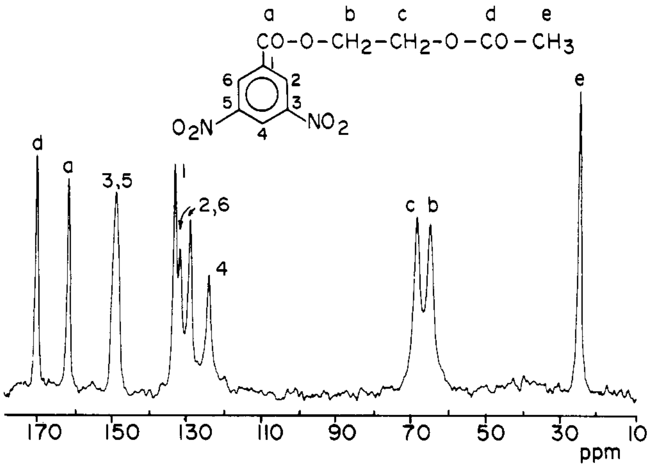

Figure 1. CP-MAS ^{13}C NMR spectrum of 2-[(3,5-dinitrobenzoyl)oxy]ethyl acetate (DNBEA).

However, even by this simple mixing, the color indicating complexation appeared.

CP-MAS ^{13}C NMR spectra of the complexes and separate components were obtained on a Bruker CXP-200 spectrometer equipped with a Doty probe. The carbon frequency was 50.307 MHz, and the cross-polarizing field was set for all samples to generate a 90° proton pulse of 3.7 μs. The spinning was in the range of 4 kHz, completely eliminating spinning side bands. Chemical shifts were measured by using an internal reference of cross-linked polyethylene. To measure $T_{1\rho}$H, a pulse sequence with increasing contact times was employed. This pulse sequence was described and applied to polymer blends for the first time in 1981.[15] It consisted of a 90° pulse for the proton, followed by decoupling. The carbon was subjected to a variable-length contact pulse, and then acquisition took place. The sequence has the advantage that at very low contact times one can measure the magnetization buildup for different carbons, and this can help in making spectral assignments.[18] The delay between pulses was set at 15 s, the high-power decoupler was on 0.09 s, and the acquisition time was set at 0.102 s. Contact times varied between 0.25 ms and a maximum of 200 ms allowed by the hardware. For the polymer samples, there was no need for such long contact times, and the maximum was 50 ms.

Results and Discussion

Spectra were first recorded and analyzed for the homopolymers, copolymer, and blend, but the main result, apart from differences in $T_{1\rho}$H values, was an apparent broadening of all signals accompanied by rather small chemical shift differences. To explain this, model compound spectra were recorded, and they will be presented here first.

Figure 1 presents the CP-MAS ^{13}C NMR spectrum of DNBEA. The assignments are given in the figure and are established by comparison with the solution spectrum of this substance.[10] The main differences between the solution and solid spectra of DNBEA consist in splittings of nonequivalent aromatic carbon signals in the solid state due to hindered rotation between C(a) and C(1). Hence, aromatic carbons 2 and 6 resonate at 128 and 131 ppm (at this stage one cannot say which is which), while carbons 3 and 5 are less different, but the signal at 150 ppm has a double width compared with that belonging to carbon 1, for example. Confirmation of the assignment is made by magnetization buildup at low contact times, when nonprotonated carbon signals are growing much more slowly than protonated carbon ones.

Figure 2 presents the CP-MAS ^{13}C NMR spectrum of NECMA. As for DNBEA, the assignments are made by comparison with the solution spectrum.[10] In this case, the two aromatic rings are different because of the substitution pattern, and, as expected, there is less resolution in the spectrum taken in solid state. The methyl (e) appears as a doublet for unknown reasons, and most of the resonances in the aromatic region contain more than one carbon atom. It is important to mention that both carbonyl signals bonded to the methyl group resonate at the same frequency in DNBEA and in NECMA (171 ppm).

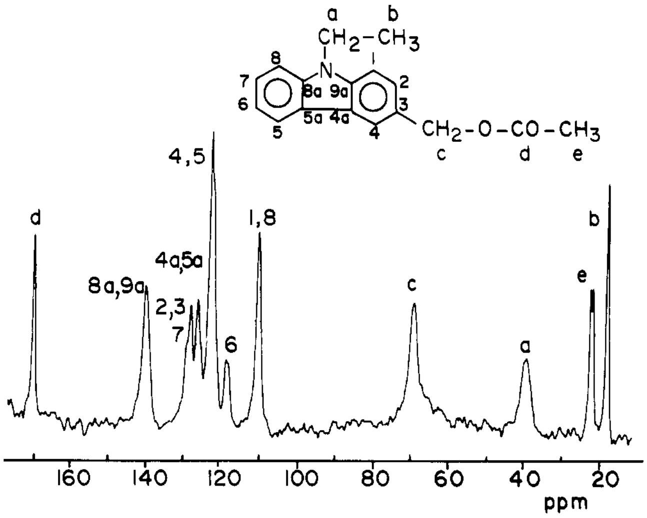

Figure 2. CP-MAS ^{13}C NMR spectrum of (*N*-ethylcarbazol-3-yl)methyl acetate (NECMA).

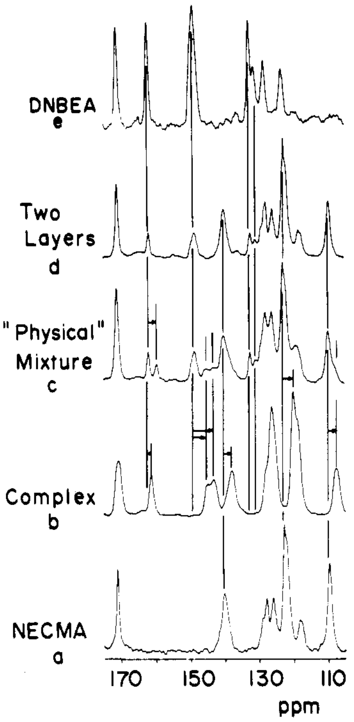

Figure 3. CP-MAS ^{13}C NMR spectra (aromatic and carbonyl regions) of (a) NECMA; (b) a 1:1 NECMA:DNBEA complex obtained by slow evaporation of THF; (c) a "physical" mixture of NECMA and DNBEA (obtained as described in the Experimental Section); (d) a sample composed of two separate layers, one of NECMA and one of DNBEA; (e) DNBEA.

To analyze what happens to the chemical shifts of different carbons when complexation occurs, Figure 3 presents a series of spectra of complexed and uncomplexed models (aromatic region). Figure 3a is the spectrum of NECMA; Figure 3e is the spectrum of DNBEA. Figure 3b presents the spectrum of the powder complex obtained by slow evaporation of the THF, while Figure 3c shows the spectrum of the intended physical mixture of NECMA and DNBEA. It is clear from the appearance of the color, as well as from the complexity of the spectrum in Figure 3C, that this is not only a physical mixture; therefore, another spectrum was taken in which the two models were introduced in the spinner as separate layers. One can see at the interface formation of complex by color appearance, however, there is very limited contact between the donor and the acceptor, making the concentration of the complex negligible. This spectrum is presented in Figure 3d. The first conclusion to be drawn when analyzing Figure 3 is that indeed there is only one signal for the CO–CH_3 carbonyl at 171 ppm in both the "physical" mixture and the two-layered sample. This makes things easier to align and minimizes chemical shift errors. As expected, the spectrum of the two-layered sample is the sum of the spectra of the two components, and this was run only for confirmation. There are, however, important differences in both b and c of Figure 3. The physical mixture (Figure 3c) can be considered as a mixture of DNBEA, NECMA, and a complex of the two. The fact that separate individual components are also present can be inferred from the appearance of the signals of NECMA and DNBEA. New signals in this spectrum can be assigned to the complex. For instance, the new signal at 160 ppm can be considered as belonging to the aromatic carbonyl of DNBEA shifted by 3 ppm upfield upon complexation. Similarly, the aromatic carbons 3 and 5 seem shifted upfield in a manner that is better seen in the spectrum of the complex. In Figure 3b, this signal is split into two parts (the two carbons become nonequivalent) and shifted upfield by 5 and 3 ppm, respectively. All signals in Figure 3b are broader than in the spectra of individual components, including the CO–CH_3 carbonyl. All signals are definitely shifted when compared to the spectra of DNBEA and NECMA, and the shift is upfield for both components. The signal belonging to the aromatic 3 and 5 carbons of DNBEA at 145 and 147 ppm can also be found in the spectrum of the physical mixture as a complex component. The signals of aromatic carbons 1 and 8 of NECMA are shifted upfield by 2 ppm, and they seem to appear as a shoulder in Figure 3c also. It is more difficult to precisely explain what happens in the area between 115 and 130 ppm, because of the many overlapping signals, but it is clear that both the shape and the relative intensities are changed. The aromatic carbonyl of DNBEA is shifted upfield but to a lesser extent than in Figure 3c. Even the signal of the aromatic carbons 8a and 9a of NECMA is shifted upfield.

These data suggest that complexation does indeed have as an effect an overall change in chemical shifts, but unlike the previous published case,[7] where a downfield shift is postulated for the donor carbons, all the signals seem to be shifted upfield due to aromatic shielding effects of stacked aromatic structures.[9] The only signal that is almost insensitive to complexation in this region is the CO–CH_3 carbonyl, which is not supposed to participate in charge-transfer interaction.

Table I

$T_{1\rho}H$ Values (ms) for Samples Presented in Figure 3

sample	NECMA carbons	DNBEA carbons
NECMA	413	
DNBEA		213
complex obtained by slow evaporation	92	92
"physical" mixture	245	150
two layers	305	202

Measurements of $T_{1\rho}H$ for the spectra presented above are summarized in Table I. $T_{1\rho}H$ values are an indication of the length of the diffusion paths: the lower the $T_{1\rho}H$ value, the lower this length. For an individual substance at a certain frequency and a certain cross-polarization field, this parameter is considered to be constant. For mixtures (and the most commonly investigated are polymer blends), one can sometimes measure two values for the two components, indicating absence of spin diffusion between components and therefore absence of intimate mixing. A single value, usually intermediate between those of the pure components, demonstrates spin diffusion between components, i.e., intimate mixing.[15] This can be the basis of analysis of the data in Table I. NECMA has a $T_{1\rho}H$ value of 413 ms, while for DNBEA it is 213 ms. The charge-transfer complex obtained by slow evaporation (spectrum in Figure 3b) has a single $T_{1\rho}H$ value of 92 ms for all the carbon signals. This decrease can be an indication that the two molecules are in close contact in the complex (shorter diffusion distances). The slow evaporation complex is an approximation for a pure 1:1 crystalline complex of the two components. Its relaxation behavior would be obviously different from the relaxation of the two components taken separately. One can assume that the charge-transfer interaction would play a very important role in the relaxation behavior of this complex. We are now attempting to grow such crystals and measure their $T_{1\rho}H$ values. As presented later in this paper, the depression of the $T_{1\rho}H$ value in the charge-transfer complexes appears also in polymers and is probably due to charge-transfer interactions. In the two-layered sample, carbons belonging to NECMA relax differently from carbons belonging to DNBEA, with the individual values slightly lower than the original ones. Values are even lower for the physical mixture, but what happens there is a bit more complicated. Subjecting the sample to extremely fast spinning generates a certain amount of heat and subjects the contents of the spinner to pressure. Therefore, during the measurement, which takes place during ca. 20 h, more and more molecules of NECMA and DNBEA come in contact and produce complexed molecules. This is obvious when the intensity of the signals from the complex is measured and plotted against contact time (to determine $T_{1\rho}H$). These signals actually *increase* in time, rendering the measurement meaningless. This can be an explanation also for the decrease of the measured $T_{1\rho}H$ values of NECMA and DNBEA in the mixture (the actual value is probably the same, but the concentration of uncomplexed molecules slowly decreases during the measurement).

Going back to the homopolymers, copolymer, and blend, Figure 4 presents their CP-MAS ^{13}C NMR spectra (aromatic region), and the chemical shift differences in the interacting systems as compared with the homopolymers are not so great. First, all the signals are rather broad, with even the CO–main chain carbonyl resonating at the lowest field. This can be due to molecular weight polydispersity (no control of the molecular weight is exerted in the radical polymerization procedure). Some other broadening of the signals in the spectra of the copolymer and blend can be due to partial complexation. All the lines are wider than 3 ppm, and some exceed even the 5 ppm maximum limit of upfield shifts observed in the model complexes. Therefore, partial complexation will create a new polydispersity of the material. Some resonances for which there seem to be obvious change are the aromatic 3 and 5 carbons signal of poly(DNBEM) and the aromatic 1 and 8 carbons signal to poly(NECMM), which considerably broadens in the copolymer (Figure 4c) and blend (Figure 4b) spectra. The most important change is the appearance of an extended shoulder at ca. 130 ppm that does not come from any of the homopolymers. In terms of chemical shifts, this is probably all that can be said about these

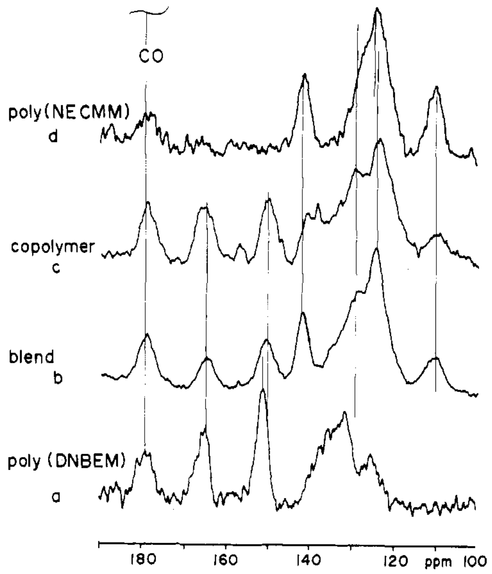

Figure 4. CP-MAS ^{13}C NMR spectra (aromatic and carbonyl regions) of (a) poly(DNBEM); (b) a 1:1 poly(NECMM):poly(DNBEM) blend; (c) 1:1 poly(NECMM-*co*-DNBEM); (d) poly(NECMM).

samples at this stage. Monodisperse samples and monodisperse copolymers (in composition) will probably generate much clearer spectra. A possibility to decompose signals in overlapping components was recently suggested for poly(methyl methacrylate).[19] The α-methyl signal of different stereosequences has different values of T_1C, making it possible to almost separate each of them at different delay times. If this is true for our homopolymers, copolymer, and blend, an initial delay could be introduced in the pulse sequence to obtain some decomposition of the broad signals.

Measurements of $T_{1\rho}$H for the samples presented in Figure 4 give much lower values than for the models. This is typical for large noncrystalline molecules and implies shorter path lengths for spin diffusion. The $T_{1\rho}$H value for poly(NECMM) is 47 ms and for poly(DNBEM) is 22 ms. There is a single $T_{1\rho}$H value for all carbons of the 1:1 blend, indicating the existence of a monophasic system, as expected.[11] This value is 27 ms. Also, one value is found for the 1:1 copolymer: 22 ms. When plotted on a graph against copolymer (blend) composition, both these values show a negative deviation from the additivity line. Figure 5 presents this plot together with a similar plot of the glass transitions of these samples. For the glass transition values, according to Kwei's equation[2] the positive deviation can be directly correlated with the extent of interaction by the term q. *In a copolymer, according to Couchman's* equation[3] the positive deviation will appear from a rather high value of a glass transition of a purely alternating copolymer. This high value has to be due to a strongly interacting intramolecular system. However, one must assume that a copolymer also presents intermolecular interactions, and from this point of view it can be treated almost as a blend. The fact that the glass transition of the copolymer is higher than that of the blend with the same chemical composition clearly indicates the existence of both intra- and intermolecular complexation in the copolymer. To our knowledge, there is no empirical equation in the literature that would consider both these parameters and their influence on the glass transition value.

The deviation in the additivity line of the $T_{1\rho}$H values is negative in both cases, and this means that even shorter distances are required for spin diffusion than would be necessary if the two components of the blend (or the two structural units of the copolymer) were just physically mixed. Again, a higher deviation is observed for the copolymer than for the blend. Of course, this shortening of the spin diffusion distance should be directly correlated with the relaxation mechanism. It is reasonable to assume that the interacting groups, attached through spacers to the main chain and therefore having a higher mobility, are the determining entities in the relaxation mechanism of these polymers. They are presumably more mobile than the α-methyl protons in poly(methyl methacrylate), which determine the relaxation in a blend with poly(styrene-*co*-acrylonitrile).[14] At this stage of the research we do not have enough information to correlate and quantify the relation between the depression in the $T_{1\rho}$H value from the additivity line and charge-transfer interaction. We are investigating a series of copolymers and blends of various compositions in an attempt to establish such a relation.

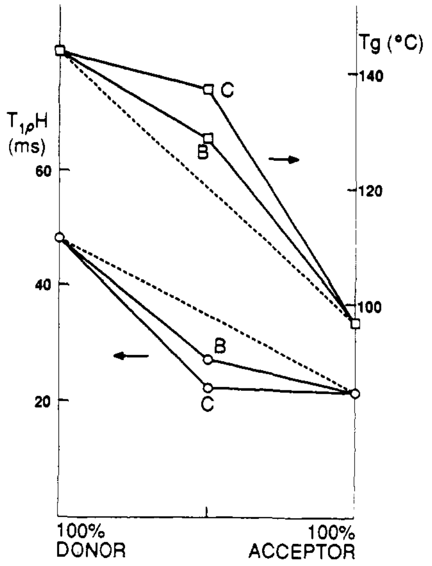

Figure 5. Plot of $T_{1\rho}$H and T_g dependence on blend (B) or copolymer (C) composition for the samples presented in Figure 4.

Conclusions

Charge-transfer complex formation has as a consequence upfield chemical shifts in the compounds analyzed in this paper. No downfield shifts are observed for the donor model or structural unit. This is probably due to formation of stacked donor–acceptor structures, where aromatic shielding effects prevail over the electron density change produced by charged transfer. Most carbons are involved in complex formation shift, and the magnitude of these shifts seems to be higher for the acceptor than for the donor. For the acceptor, the electron density change is of the same sign as the aromatic shielding effect, while for the donor they are of opposite signs. However, the shifts are rather small in the case studied here (1–5 ppm) and hence are almost unobservable in the polymer spectra, where all lines are broad. When a complex is formed, either for the model compounds or in a polymer system, a single $T_{1\rho}$H value can be measured. This value does not seem to be intermediate between the values found for the individual components; it seems to be lower. We believe that the depression of the $T_{1\rho}$H of the complex is related to charge-transfer interaction, in the same way as is the increase of the glass transition temperature in copolymers and blends.

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Registry No. (NECMM)(DNBEM) (complex), 103515-28-2; NECMA, 122624-68-4; (NECMM)(DNBEM) (copolymer), 122624-70-8; DNBEA, 80880-32-6; DNBEM (homopolymer), 82008-07-9; NECMM (homopolymer), 67549-45-5; NECMA·DNBEA, 122624-69-5.

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Poly(vinylnaphthalene peroxide)s: Syntheses, Characterization, and Thermal Reactivity

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ABSTRACT: Three new polymeric peroxides based on vinyl and substituted vinylnaphthalenes have been synthesized and characterized. The thermal reactivity of these polymers was studied by DSC and PGC. The $\Delta H_{\mathrm{d}}^{\circ}$ values of these polymers are close to or slightly higher than the earlier reported PSP. They are also powdery materials and are superior autocombustible fuel.

Introduction

Not long ago, Cais and Bovey reported on the chain flexibility and molecular dynamics of poly(styrene peroxide) (PSP),[1] an effort undertaken for the first time to study the physicochemical properties of polymeric peroxides, which had thus far received attention[2,3] only in regard to their intermediacy in the inhibition by oxygen in vinyl polymerization. Recently, studies from our laboratory on polymeric peroxides have been of the former nature and were successful in providing a thermochemical explanation for the unusual, exothermic, thermal degradation of these polymers.[4,5] Application of this characteristic exothermic degradation of these polymers has resulted in detecting a unique phenomenon of autopyrolysis in PSP,[6a] which has caused it to be considered as a candidate for a specialized fuel of the future.[6b] The property of autopyrolysis exhibited by these polymers is due to their unusual, highly exothermic heats of degradation.

An evaluation of the heats of degradation of different polymeric peroxides is out of question for want of data. The number of polyperoxides reported so far is only about a dozen,[3] and even these, except for one or two, have hardly been characterized. Under the circumstances, it seemed desirable to prepare new polyperoxides in view of their potential as highly exothermically degrading materials. By a comparison of the available heats of degradation of PSP[4] and poly(methyl methacrylate peroxide) (PMMAP)[5] (the former being higher), it was thought best to try aromatic monomers for making new polyperoxides. Hence, vinyl and substituted vinylnaphthalenes were chosen. In this paper, we describe the syntheses, characterization, and thermal reactivity of three new polyperoxides. Conforming to expectations, all these polymers exhibited equal or slightly higher heats of degradation than PSP. They were powdery materials, thus affording easier handling and use compared to the earlier reported PSP, a sticky semisolid polymer under ambient conditions.

Experimental Section

Preparation of Monomers. 2-Vinylnaphthalene was prepared from 2-acetonaphthone (Fluka AG) by reduction with $NaBH_4$ followed by dehydration of the resulting secondary alcohol with iodine and benzene under reflux for 0.5 h. 1,α-1-(α-methylvinyl)naphthalene and 2-(α-methylvinyl)naphthalene were prepared from 1-acetonaphthone (Fluka AG) and 2-acetonaphthone, respectively. The naphthones were subjected to Grignard reaction with CH_3MgI, and the resulting tertiary alcohols were dehydrated by stirring benzene solutions of them with *p*-toluenesulfonic acid overnight. All the monomers were purified by column chromatography (silica gel; petroleum ether).

Polymerization. The polymeric peroxides were prepared by passing a copious flow of oxygen through benzene solutions of monomers in glass cells fitted with a sintered funnel at the bottom for passing gas and placed in a water bath at 50 °C. This cell assembly provides intimate mixing of oxygen with the monomers and also constant stirring. AIBN (0.02 mol %) was used as the initiator. The polyperoxide of 2-vinylnaphthalene was formed in 12% yield by passing in oxygen for 48 h; those of 1- and 2-(α-methylvinyl)naphthalenes were formed after 100 h each, in 15% yield. The polymers were precipitated by using petroleum ether and purified by several reprecipitations.

Analysis. All NMR spectra were recorded in $CDCl_3$ at ambient temperature: ^{1}H NMR spectra on a Varian T-60 (60 MHz) or a Bruker FT-270 spectrometer (270 MHz) and ^{13}C NMR spectra on a Bruker FT-270 spectrometer (67.89 MHz) under broad-band

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