radicals $\cdot CH_xCl_{3-x}$ formed from the solvent in the charge-transfer process, are present in considerable amount.

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Laser Flash Photolysis Study of Polymers Containing Benzoyl and Naphthalene Groups

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ABSTRACT: The photochemistry of copolymers of phenyl vinyl ketone, 2-vinylnaphthalene, and methyl methacrylate has been examined by laser flash photolysis techniques. Triplet energy transfer from the initially excited benzoyl chromophores to the naphthalene groups occurs by two distinct mechanisms which reflect static transfer and dynamic transfer. The former occurs between close neighbors along the chain, as well as when loops in the polymer bring together donor and acceptor molecules. Dynamic processes involve the diffusion of segments within the polymer and take place in the 10^{-6}–10^{-7}-s time scale at room temperature.

Introduction

The photodegradation and photooxidation of many common polymers, as well as the photocuring of organic coatings, are frequently controlled by chromophores which absorb in the near-ultraviolet or visible region. The importance of this spectral region is also reflected in the area of polymer stabilization, where many photostabilizers work by either screening the near-ultraviolet light or scavenging the intermediate (usually excited states or radicals) produced on excitation.[4] Since those chromophores are usually a minor component in the polymer system, their efficiency is largely determined by the probability that the mobility of the macromolecule and/or energy migration will bring the excited chromophore and the reactive site together. In order to examine both energy transfer and the mobility of excited states in macromolecules, we have studied the photochemistry of a series of copolymers of phenyl vinyl ketone, 2-vinylnaphthalene, and methyl methacrylate. In these systems the light from a nitrogen laser (337.1 nm) is absorbed virtually exclusively at the benzoyl site, which can then transfer the energy to yield the easily detectable naphthalene triplet.[5]

The transfer of triplet energy from aromatic carbonyls in polymers to bound and free naphthalene moieties has been examined before in solution[5-8] and at 77 K,[9-11] but the kinetics of the intramolecular energy transfer process had not been examined directly.[12] Our study reveals the importance of static and dynamic phenomena in the energy transfer process. Energy migration between carbonyl chromophores, which plays an important role in many other systems,[13-18] does not seem to contribute significantly in the copolymers examined in this study.

Results

All the results reported in this paper have been obtained under oxygen-free conditions, using laser flash photolysis

Table I
Composition of the Copolymers Studied

sample no.	% ketone[a]	% naphthalene[a]	$[\eta]$[b]	$\overline{M}_w$[c]
1	21.3	0	86.63	328 000
2	12.5	1.6		
3	15.3	2.6	119.8	510 000
4	16.7	2.1	127.7	555 000
5	13.2	3.5	114.0	478 000
6	7.1	1.4		
7	7.6	2.6		
8	8.4	3.9		
9	10.9	0	127.3	553 000
10	4.6	1.5		
11	4.9	2.9	110.1	457 000
12	4.9	3.9		

[a] From UV spectroscopy; see text. [b] In mL/g. [c] Calculated by using literature parameters for poly(methyl methacrylate): Bransdrup, J.; Immergut, E. H., Eds. "Polymer Handbook": Wiley: New York, 1975; p IV-139.

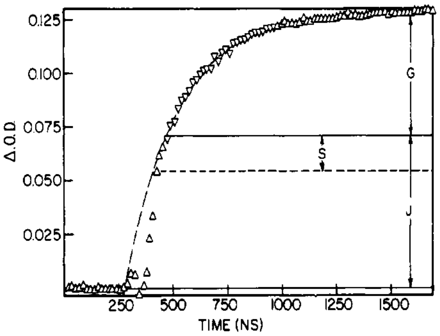

Figure 1. Trace for polymer sample no. 4 in benzene (22 °C, 430 nm), showing *J* and G as well as the carbonyl contribution to *J* (labeled *S*), estimated by using sample no. 9. The inverted triangles show the data used to calculate the kinetics (laser fired at t = 360 ns).

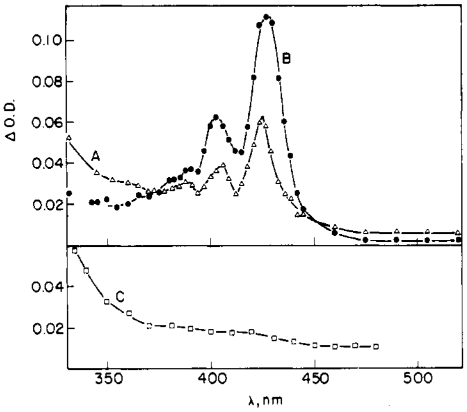

Figure 2. Transient spectrum observed immediately after the laser pulse (A, △) and after 1.5 μs (plateau region, B, ●) for sample no. 4 in benzene. Also included in the figure (C, □) is the spectrum from poly(phenyl vinyl ketone-*co*-methyl methacrylate).

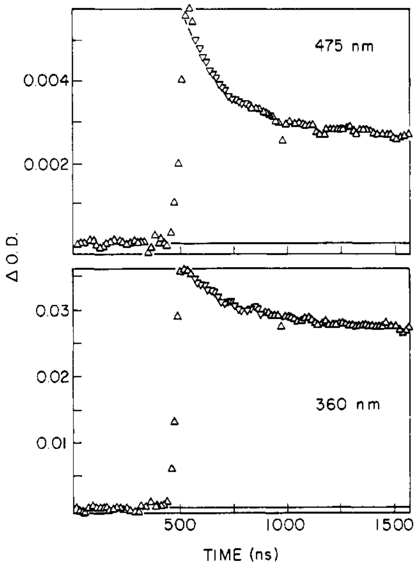

Figure 3. Traces obtained with sample no. 4 in benzene at wavelengths where the triplet carbonyl absorbs more strongly than the naphthalene triplet.

techniques and employing for excitation the pulses from a nitrogen laser (337.1 nm, 8 ns, 3 or 10 mJ) for excitation. The composition and molecular weight of the polymers used are described in Table I. In all cases the main component of the polymer is methyl methacrylate (78.7–93.9%), with ketone moieties in the 4.6–21.3% range and naphthalene moieties in the 0–3.9% range. The samples were prepared by free radical copolymerization of mixtures of methyl methacrylate, phenyl vinyl ketone, and 2-vinylnaphthalene; their composition is based on the comparison of their UV spectra with those of isobutyrophenone and 2-ethylnaphthalene. Molecular weights were estimated from viscosity measurements, using the constants for poly(methyl methacrylate).

When solutions of the samples in Table I are excited with the laser pulses, the transient phenomena observed clearly reveal the occurrence to two distinct processes. A typical trace obtained with sample no. 4 in benzene is shown in Figure 1; a first-order growth is preceded by an initial jump. The growth reflects the formation of triplet naphthalene moieties, as the transient spectrum in the plateau region clearly reveals (vide infra), while the initial jump is also the result of formation of triplet naphthalene, superimposed upon the absorption due to the carbonyl triplet. Figure 2 illustrates the effect. The spectrum in the plateau region corresponds to the naphthalene triplet moieties[5] (slightly red-shifted with respect to that for naphthalene itself), while the one immediately after the laser pulse is superimposed on the absorption observed in samples of poly(phenyl vinyl ketone-*co*-methyl methacrylate), also illustrated in the same figure.

The trace shown in Figure 1 is a truly representative example; the same effect is observed in a variety of copolymers in different solvents and over an extensive temperature range. For practical purposes the trace can be divided into a static component ("jump") and a dynamic contribution ("growth"). The latter is in a way more informative, since it reflects the mobility of segments within the polymer, and our work has been largely centered on this aspect of the problem, though admittedly, our emphasis in the dynamic phenomena may be somewhat influenced by the fact that measurements are more precise in this case and interpretation of the data is somewhat simpler than in the case of static processes.

The decay of the triplet naphthalene moieties is a relatively slow process. At low light intensities it follows clean first-order kinetics and lifetimes in the neighborhood of 30 μs are not uncommon; these may, to some extent, be determined by quenching by minor impurities in the solvent and/or copolymer.

The signals due to the naphthalene triplet are, in general, so intense as to prevent a detailed study of the behavior of the carbonyl chromophores in the copolymers, since the T–T absorptions in these are relatively weaker. Only in the regions below 370 nm, or over 470 nm, can the

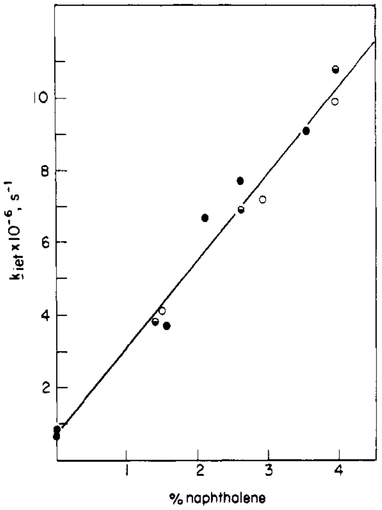

Figure 4. Effect of polymer composition on the values of k_{iet} at 22 °C in benzene. The points have been identified according to their carbonyl content: (●) over 12%; (◒) between 7 and 9%; (○) below 5%.

carbonyl triplet decay be examined, although in the latter region their absorption is also rather weak. Figure 3 illustrates the behavior of the carbonyl triplet; residual absorbances after triplet decay are due to the naphthalene triplet.

Effect of Polymer Composition. The kinetics for the growth of triplet naphthalene following excitation of the carbonyl groups is sensitive to the polymer composition; Figure 4 shows the dependence of the first-order rate constant for intramolecular energy transfer (k_{iet}) on the abundance of naphthalene groups for a series of experiments in benzene at 22 °C. The points have in turn been identified according to their carbonyl content. Quite clearly the rates correlate with the naphthalene content but *not* with the abundance of carbonyl groups.

The relative importance of static and dynamic phenomena seems to be only slightly dependent upon the polymer compositions. For practical reasons it is convenient to define a "jump-to-growth ratio", hereafter referred as J/G, as the ratio of the change in absorbance observed as a "jump" to the "growth" segment of the trace. For most of the samples J/G at 430 nm is between 1.3 and 1.5, with the exception of the two polymers with 3.9% naphthalene (see Table I), where the average value is 2.2. Therefore, the composition changes that bring about a threefold increase in k_{iet} only change J/G by ~35%. Both J and G seem to be largely controlled by the same factors.

It is important to note that J/G does not fully reflect the relative importance of static and dynamic phenomena but, rather, it overweights the importance of the jump. This is due to the fact that the initial jump can include up to 30% absorbance due to the carbonyl triplet; in addition, the carbonyl triplets disappear during the growth part of the trace, and as a result the absorbance due to triplet naphthalene effectively compensates for the decay of the carbonyl absorption. In other words a more realistic estimation of the ratio of static-to-dynamic phenomena would subtract the carbonyl absorption from the jump and add it to the growth. Unfortunately, an estimation of the fraction of absorbance due to the carbonyl is not always easy; a rough estimate would, however, suggest that for $J/G \sim 1.3$ about 60–65% of the naphthalene triplets are generated in dynamic quenching processes.

We note (Figure 4) that for copolymers containing 2% or more of naphthalene groups the value of k_{iet} reflects over 90% quenching, and we will, in these systems, disregard the independent decay of carbonyl triplets.

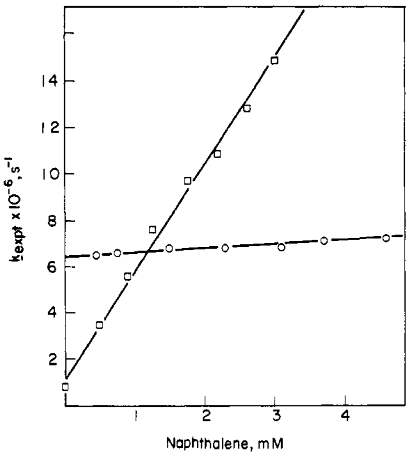

Figure 5. Dependence of the triplet lifetime (benzene, 22 °C) on the concentration of polymer (○) for polymer sample no. 4 and intermolecular triplet quenching (sample no. 1) by 2-ethylnaphthalene (□).

Concentration Dependence and Intermolecular Energy Transfer. In order to study intramolecular energy transfer in a polymer, it is important to establish that the rate constants measured are independent of the bulk polymer concentration, in other words, that the results have been obtained close enough to the "infinite-dilution" limit that energy transfer between different macromolecules can be ignored. Figure 5 shows the dependence of the rate constants for the buildup of naphthalene absorption as a function of the bulk concentration of naphthalene moieties for polymer sample no. 4 in benzene at 22 °C. The "effective" bimolecular rate constant is in this case $\sim 1.9 \times 10^8$ M^{-1} s^{-1}, as determined by the slope of the corresponding plot. The reasons for this apparently low rate are related to the fact that several naphthalene moieties are attached to each polymer molecule (see Discussion). All experiments, other than the ones in this subsection, have been carried out close enough to the intercept in Figure 5 that interpolymer energy transfer is unimportant.

Figure 5 also includes a plot for the quenching of poly(methyl methacrylate-*co*-phenyl vinyl ketone) sample no. 1 by 2-ethylnaphthalene, from which we obtain $k_q = 4.1 \times 10^9$ M^{-1} s^{-1} at 22 °C in benzene.

Effect of Laser Intensity. The excitation dose from the laser pulse was varied by a factor of ca. 20, using suitable neutral-density filters. In experiments with polymer sample no. 4 we found no significant change in k_{iet}. We also find that the changes in J/G are all within experimental error, though a slight trend of J/G to decrease with decreasing light intensity was apparent. All these experiments were carried out under conditions where only one quanta per macromolecule can be absorbed.

Solvent Effects. Since solvents influence the conformation of polymers in solution,[19] it seemed desirable to see how solvents would affect both static and dynamic phenomena in copolymers containing benzoyl and naphthalene moieties. A series of experiments was carried out with polymer sample no. 4 and Table II summarizes the results. We find that the same solvents in which the polymers are rather insoluble cause a considerable increase in k_{iet} and in J/G. Figure 6 illustrates the effect of the concentration of methanol on the value of k_{iet} in systems with benzene or acetone as cosolvent.

Temperature Effect. Experiments were carried out with polymer sample no. 5 for the intramolecular transfer (k_{iet}) and quenching of the carbonyl triplet in sample no.

Table II
Solvent Effects on the Kinetics of Energy Transfer

	sample no. 4		sample no. 1	
	k_{iet}[a]	J/G	k_{CO}[a,b]	k_q[c]
benzene	6.8×10^6	1.4	8.0×10^5	4.1×10^9
toluene	8.9×10^6	1.2	1.3×10^5	5.2×10^9
p-xylene	1.3×10^7	1.4	3.2×10^6	4.9×10^9
acetone	6.8×10^6	1.6	5.8×10^5	6.8×10^9
dichloromethane	7.6×10^6	1.4	9.8×10^5	5.5×10^9
benzene-heptane (7:3)	9.1×10^6	1.3	1.2×10^6	3.9×10^9
benzene-mesitylene (7:3)	3.3×10^7	2.2	1.3×10^7	4.4×10^9
benzene-methanol (1:1)	1.0×10^7[d]	1.8	1.4×10^6	5.2×10^9
acetone-methanol (7:3)	9.5×10^6[d]	1.5	9.3×10^5	6.0×10^9

[a] In s^{-1}. [b] Rate constant for the decay of the carbonyl triplet. [c] Quenching by 1-methylnaphthalene, in units of M^{-1} s^{-1}. [d] See also Figure 6.

Table III
Kinetic Parameters of the Processes in Toluene

process	E_a[a]	log A
decay of carbonyl triplet	3.1	8.4[b]
intramolecular energy transfer	3.8	9.9[b]
intermolecular energy transfer	2.9	11.85[c]
diffusion (expected)	3.0	

[a] In kcal/mol. [b] With A in s^{-1}. [c] With A in M^{-1} s^{-1}.

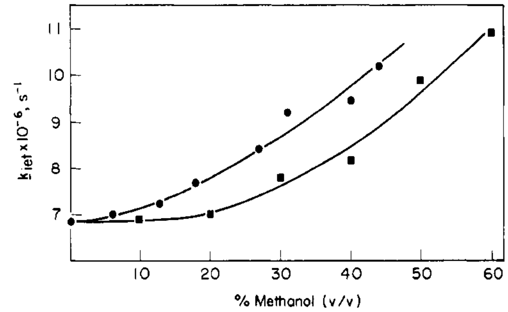

Figure 6. Effect of the addition of methanol on the kinetics of intramolecular energy transfer for polymer sample no. 4 at room temperature, using as cosolvent acetone (●) and benzene (■).

1 with 2-ethylnaphthalene in order to examine the intermolecular quenching processes (k_q). In this case the concentration of 2-ethylnaphthalene selected for the Arrhenius display of reciprocal lifetimes (Figure 7) was such that over 90% of the decay occurred via quenching rather than intrinsic decay of the carbonyl triplet. Table III shows the temperature dependence of the kinetic behavior of several species in the +22 to −94 °C range in toluene solvent; included in the same table is the activation energy expected for a diffusion-controlled process, calculated according to eq 1.[20,21]

$$E_a = -R\ \partial[\ln (T/\eta)]/\partial(T^{-1}) \qquad (1)$$

Discussion

While singlet energy transfer can occur by a variety of mechanisms, which include short- and long-range processes, triplet energy transfer can only take place by an exchange mechanism,[16,23-26] which requires close proximity of donor and acceptor. This property makes triplet–triplet transfer an excellent probe for molecular conformation and motion, since any evidence for energy transfer is in turn conclusive evidence that donor and acceptor have approached within a few angstroms. In addition, the relatively long lifetime of triplet probes makes the study of microsecond phenomena viable. Indeed, the reactivity of carbonyl triplet probes has been extensively used by Breslow and Winnik to study molecular conformation and chain flexibility in benzophenones substituted with long hydrocarbon chains.[27,28] Similar types of studies have recently been extended to micellar systems.[29] In fact, it is in a way surprising that our results would resemble so much the subdivision in static and dynamic phenomena which is so common in quenching processes in micellar systems;[30,31] while in these systems, there is a relatively clear distinction between being "inside or outside", it is not the same case in *intramolecular* polymer processes. The evidence indicates, however, that a quencher molecule can be within reach for a formally "instantaneous" transfer; otherwise it belongs to a group that will have to undergo diffusion to reach the excited donor. The division between these two cases is a sharp one, which apparently requires no intermediate situations. One of the factors contributing to this effect is naturally the strong dependence of the rate for electron exchange energy transfer with the distance between donor and acceptor ($k \propto R^{-6}$).[24]

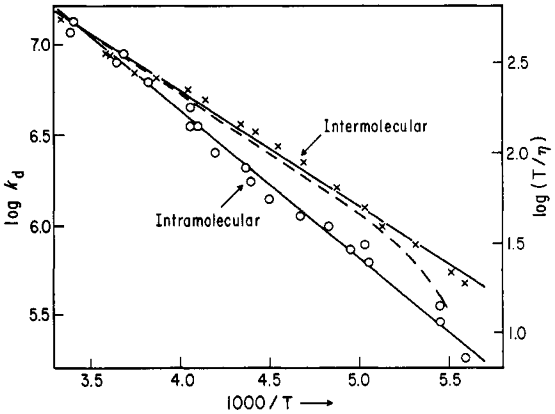

Figure 7. Arrhenius plot of the rate constant for the formation of naphthalene triplets in toluene using polymer sample no. 5 (○) and for an intermolecular case (×) using polymer sample no. 1 and 2-ethylnaphthalene; the concentration of the latter was chosen so that at 22 °C the first rate constant would match that of the intramolecular case. The dashed line (right scale) corresponds to the variation of viscosity (as log (T/η)) with $1000/T$.

The dependence of the rate constant k_{iet} upon the composition of the copolymers provides an interesting insight into the mechanism of energy transfer. The values of k_{iet} depend linearly upon the concentration of naphthalene, as one would expect (Figure 4).[32] A concentration of naphthalene moieties of ca. 0.32% would be enough to cause 50% decay via quenching; formally, each naphthalene moiety will visit some 300 monomer units during the lifetime of the carbonyl triplet in benzene at 22 °C. The values of k_{iet} are independent of the relative abundance of carbonyl chromophores; we take this observation to mean that energy migration between carbonyl chromophores does not make an important contribution to the energy transfer process. Energy hopping between sequential carbonyl chromophores is known to take place whenever two or more carbonyls are next neighbors or nearby neighbors; however, this must effectively "lock" the energy within a limited segment of the molecule, thereby minimizing its contribution to the transfer process.

The rate constant for energy transfer from carbonyl groups in polymers to free 2-ethylnaphthalene (4.1×10^9 M^{-1} s^{-1} at 22 °C in benzene based on the slope in Figure 5) seems normal for a transfer of this type and is slightly lower than that for similar processes between small molecules.[33] By constrast, the transfer between two copolymers occurs with an apparent rate constant of 1.9×10^8 M^{-1} on a *per naphthalene moiety* basis (circles in Figure 5; note the small slope); however, if we take into consideration that every macromolecule has roughly 100 naphthalene moieties, we find that the rate of transfer between two polymer molecules somewhat exceeds 10^{10} M^{-1} s^{-1}, this being faster than between a macromolecule and a small molecule. Quite clearly, the increase in size compensates for the decrease in diffusion coefficient. This is naturally a rather simplistic view, which ignores the fact that the smaller macromolecules in the distribution may be the more efficient quenchers, as well as any possibility of macromolecular entanglement.

Solvent effects reveal the importance of conformation in determining the kinetics of energy transfer, as well as the relative importance of static and dynamic phenomena. The solubility of the polymers increases in the order mesitylene < *p*-xylene < toluene < benzene, and k_{iet} decreases with increasing polymer solubility. As the polymer becomes more soluble, it also stretches or expands considerably and, as a result, the average distance between energy donors and quencher groups increases. The same effect is revealed in cases where methanol is used as cosolvent (Table II and Figure 6). Interestingly, J/G also increases in solvents where the polymer is less soluble; this is conclusive evidence that at least part of the static process results from transfers between segments which are located at a considerable distance along the chain but relatively close in space. If static processes involved *solely* close neighbors in the chain, the process would be expected to be solvent independent.

The temperature dependence of k_{iet} in toluene indicates that transfer of energy within the polymer occurs with a higher activation energy than the intermolecular process, the latter being essentially a reflection of the temperature dependence of the viscosity of toluene. The results indicate that the diffusion of segments of the polymer, which is necessary for the transfer to occur, is hindered by the local environment, resulting in an increase in E_a; the rather low preexponential factor also seems consistent with the assumption of considerable steric hindrance.[34]

Conclusion

This study of energy transfer between aromatic carbonyl and naphthalene moieties in copolymers with methyl methacrylate reveals the importance of static and dynamic phenomena in determining the efficiency and kinetics of transfers of this type. Static phenomena occur between donor–acceptor pairs which are in close proximity at the time of excitation and includes close neighbors in addition to formally remote pairs brought together by loops in the polymer conformation.

Dynamic phenomena occur as a result of the diffusion of segments within the copolymer which brings together the donor and acceptor in processes which occur in the 10^{-6}–10^{-7}-s time scale; by contrast, transfers between identical or very similar next neighbors is known to occur in the 10^{-10}–10^{-12}-s time domain. The difference emphasizes the importance of distance in energy transfer by the exchange mechanism.[23,24]

Experimental Section

Materials. Phenyl vinyl ketone was prepared from β-chloropropiophenone (Aldrich) by a literature procedure.[35] Methyl methacrylate (K&K) was treated with base, dried, and distilled and 2-vinylnaphthalene (Aldrich) was used as received. All polymerizations were initiated with azobis(isobutyronitrile) and the polymers were separated before the conversions reached 15%. The copolymer compositions were determined by comparing their spectra with those for 2-ethylnaphthalene and isobutyrophenone; in general, the abundance of phenyl vinyl ketone moieties in the polymer always exceeds its abundance in the polymerizing mixture. All polymer samples were precipitated with methanol and redissolved in benzene five times; finally, they were freeze-dried from benzene.

Solvents were Aldrich Gold Label or Fisher of the highest available grade and were used as received.

Laser Flash Photolysis. The samples were excited with the pulses (337.1 nm, 8 ns, 3 or 10 mJ) from a Molectron UV-400 or UV-24 nitrogen laser. The two instruments used are of similar design and employ a pulsed xenon lamp as monitoring source, a B&L or PRA-B204 monochromator, and RCA-4840 photomultipliers. Both instruments have been fully interfaced with PDP-11 computers. Further details have been reported elsewhere.[36]

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References and Notes

(1) Radiation Laboratory.
(2) National Research Council of Canada, where correspondence should be addressed.
(3) This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy and by the National Research Council of Canada. This report has been issued as NRCC-18875 and NDRL-2175.
(4) The number of papers and patents in this area is so large that the authors are reluctant to choose a few as representative references; a book on the subject and the proceedings of a recent conference can provide an overview of the subject: Ranby, B.; Rabek, J. F. "Photodegradation, Photooxidation and Photostabilization of Polymers"; Wiley: London, 1975. *Org. Coat. Plast. Chem.* **1980**, *42* (contains papers presented at the 179th National Meeting of the American Chemical Society, Houston, Texas, 1980).
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Causes of Haze of Low-Density Polyethylene Blown Films

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ABSTRACT: Static and on-line haze, low-angle light scattering, and microscopic measurements have shown that haze of low-density polyethylene (LDPE) blown film is caused mainly by scattering from rough film surfaces. The rough surfaces are formed by two mechanisms, one involving melt flow disturbances at the die exit and the other caused by stress-induced crystallization close to the film surface. Haze arising from melt flow disturbances can be reduced by selecting resins that contain relatively low concentrations of large molecules and by intense mechanical deformation of the melt before extrusion. Mechanical deformation reduces melt elasticity and haze by a reversible physical mechanism that generates a long-lived nonequilibrium melt structure. Haze arising from crystallization may possibly be reduced by introducing more irregularity into the polymer chain by copolymerization or by increasing short-chain branching.

Introduction

Low-density polyethylene (LDPE), made by the free radical initiated polymerization of ethylene at high pressure, is extensively used in the form of film. These films have a more or less milky white or hazy appearance caused by light scattering by the films. In spite of the importance of haze in end-use applications, there is little published information on the mechanisms and causes of haze development in films. The purpose of our work was to acquire a better understanding of the causes of haze of LDPE films, especially blown films. Improved understanding should provide a guide for modifying polymer chain structure and film fabrication conditions to achieve lower haze levels.

When a polymer film is placed in the path of a light beam, light scattering can originate from the interior of the film and from the air–film interfaces. Light scattering from the interior of films made from semicrystalline polymers has been placed on a firm theoretical and experimental basis by Stein[1] and others.[2] In most investigations, scattering from film surfaces has been reduced to negligibly low levels by coating the film with a fluid with a refractive index equal to that of the film or by crystallizing the film between smooth glass microscope slides. Light scattering from film surfaces has been much less extensively examined. However, there is general agreement that the haze of thin (~25 μm) blown LDPE film is caused mainly by scattering from rough film surfaces.[3-6]

In a classic study, Huck and Clegg[3] examined the effect of extrusion conditions on the haze of blown LDPE films. They interpreted their results in terms of two mechanisms for generating rough film surfaces. These mechanisms give rise to "extrusion haze" and "crystallization haze". In the extrusion haze mechanism, surface bumps were assumed to form on the molten film surface upon exit of the polymer fluid from the film die. The surface bumps were thought to smoothen upon moving downstream from the die until solidification of the film prevented further smoothening. Crystallization haze was postulated to occur from surface roughening caused by the formation of crystalline aggregates on or close to the surface of the film. Using these hypotheses, they rationalized many of the effects of film fabrication conditions on film haze.

A number of workers have proposed that polymer melt elasticity is closely related to blown film haze. According to Huck and Clegg,[3] the haze of LDPE film increases as extrudate die swell increases. Shroff et al. used entrance pressure drop upon flow into a capillary, P_0, as a measure of melt elasticity and concluded that the haze of blown poly(ethylene-*co*-vinyl acetate) film increased as P_0 increased.[7]

The effect of polymer chain structure on LDPE film haze has been only briefly investigated. Perron and Lederman concluded from GPC examination of a few LDPE resins that broadening molecular weight distribution caused an increase in haze.[4] However, no allowance was made for long-chain branching of LDPE in the analysis of the GPC chromatograms, so this conclusion is not firmly established. Foster concluded that the total haze of LDPE blown films increased as the number of long branches in the resin increased.[6]

It is well-known that the haze of LDPE film can be reduced by subjecting the polymer melt to a mechanical deformation in an intensive mixer before extrusion.[8] In the film industry this process is referred to in various ways, such as "working", "homogenization", and "shear refining".