three-dimensional controlled growth cannot be specified at present although the rate data fit the general formulation. It would appear to be premature to attempt to select the appropriate nucleation interfacial quantities that are involved. The analysis sets forth the values that are obtained and which in turn must be satisfied under a given set of conditions.

The radial growth rate of spherulites, crystallized in the bulk, can also be analyzed according to the different general types of nucleation processes.[53] It becomes a matter of interest, therefore, to compare the spherulite growth rate and that for the lamellar growth of crystals formed from dilute solution. Spherulite growth rate data for molecular weight fractions of linear polyethylene are also available from the work of Holland and Lindenmeyer[56a] and a detailed analysis of these data has already been given.[54,56b] Taking the set of equilibrium melting temperatures 145.5 and 118.6°, it is found that the slopes in the appropriate plots,[54] which directly relate to the product of interfacial energies, are 3.1 times greater for the dilute solution case, for three-dimensional nucleation. This ratio is reduced to 2.8 for a two-dimensional process. For the latter case this ratio can be reduced to 1.4 for T_s^0 of 110° and the two slopes are identical if T_s^0 is taken as 107°. However, in view of the experimentally observed solubility data and the previous discussion the latter two values for T_s^0 are not acceptable. Therefore, we can conclude quite generally, without recourse to detailed mechanisms, that the product of interfacial energies involved in dilute solution growth is much greater than for spherulites crystallizing in the bulk. Hence it is not valid to equate these quantities nor to conclude that the same growth mechanism is involved in these two cases.[36]

Melting Temperature. Given a crystallite size and an interfacial free energy, it is a straightforward procedure to calculate the melting temperature T_m for the crystals formed from dilute solution in the absence of diluent, *i.e.*, in the pure state. The appropriate expression, for the higher molecular weights, is given by eq 1 with T_m replacing T_s and T_m^0 the equilibrium melting temperature in the pure state replacing T_s^0. Taking T_m^0 as 145.5° and σ_{ec} equal to 3400 cal/mol, we find that T_m is calculated to increase monotonically from 114.9 to 126.7° as the crystallite thickness increases from 115 to 190 Å. These latter crystallite sizes correspond to dilute solution crystallization in the range 75–95°. These melting points are very difficult to measure directly because of rapid recrystallization in the melting range.[16,57] Hence, the direct experimental verification of the predicted melting temperatures must await the development of more refined experimental techniques.

An indirect estimate of the melting temperatures can be obtained from annealing experiments on the dried specimens. On heating up to a critical temperature no changes are observed in a variety of properties.[12,29,30,58,59] However, above this critical temperature various changes occur in the system including an increase in crystallite size. These changes can be attributed to partial melting and rapid recrystallization,[12,29,53] so that this temperature can serve as a measure of the melting temperature, particularly for comparative purposes.

It has been reported[60] that this critical temperature increases as the crystallite thickness increases. More specifically for an original spacing of 114 Å it was found to be 112–117°, while for crystals prepared at a higher temperature where ζ = 170 Å, this critical temperature has increased to 122–127°.[60] These values agree very well with the melting temperatures calculated by the method outlined above.

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Communications to the Editor

Charge Transfer in Donor Polymer–Acceptor Polymer Mixtures

Studies of charge-transfer complexing in polymer systems is receiving increased attention from both theoretical and practical viewpoints.[1] Diverse properties, such as electrical conductivity,[2] thermal stability,[3] absorption spectra,[4] and complex equilibria[5] have been studied. The mechanical properties of these polymeric charge-transfer materials have not been reported, since, in previous cases, complexing arose from the interaction of a donor polymer with an acceptor monomer. This, in turn, led to dark, insoluble, brittle and, in many cases, ill-defined solids. However, the polymerization of 2-vinylpyridine and 2,4,6-trinitrostyrene gave a low molecular weight copolymer with donor and acceptor species in one chain.[4] We wish to report some preliminary data describing our approach to preparing well-defined, linear, high polymers, which retain usable mechanical properties while undergoing charge-transfer complexing with each other. This report describes the synthesis of high molecular weight acceptor polymers for the first time and the synthesis of a new class of donor polymers. Their charge-transfer mixtures are also reported.

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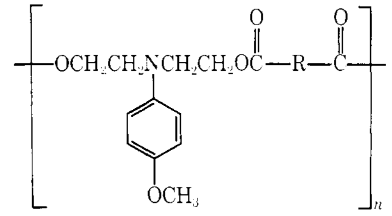
TABLE I
PROPERTIES OF DONOR POLYMER I, ACCEPTOR POLYMER II, AND A 50:50 MIXTURE

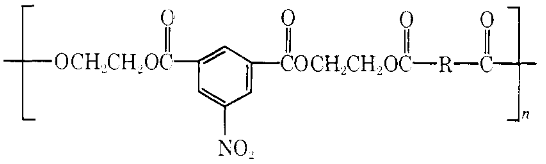
Property[a]	I	50:50 mixture[b]	II
Color	Colorless	Yellow-orange[f]	Colorless
Reduced viscosity[c]	0.80	0.60	0.40
Lowest energy absorption maximum,[d] mμ	298	398[e,f]	330
Glass transition temp (T_g), °C	50–60	60–70	70–80
Tensile modulus, psi	335,000	360,000	260,000

[a] Films prepared by solution casting from chloroform. [b] This mixture was prepared from 10% solutions (by weight) of I and II. [c] Determined in chloroform at 25° at 0.2 g/100 ml. [d] Determined on a Cary 14 spectrophotometer in chloroform. [e] Determined by scanning a mixture of solutions of I and II in a 2-cm cell against individual 1-cm cells containing I and II. [f] The possibility that the color was caused by the presence of unreacted monomers was ruled out since the individual polymers were refluxed for 3 days with methanol prior to spectroscopic study. This treatment would remove *p*-anisyliminodiethanol and the bishydroxyethyl ester of 5-nitroisophthalic acid since they are soluble, at room temperature, to the extent of 50 and 10 g in 100 ml of methanol. Based on the probable molecular weight distribution for condensation polymers obtained in high yield and molecular weight, no extraordinary amounts of low molecular weight oligomers should be present to interfere with the color measurements.

A typical donor polymer–acceptor polymer composition was prepared either by solution casting or melt mixing poly(*p*-anisyliminodiethanol bisphenol A carbonate) (I) and poly(bis(2-hydroxyethyl)-5-nitroisophthalate bisphenol A carbonate) (II). The 50:50 mixture (by weight) which gives clear, uniform and flexible films, possesses a bright yellow-orange color. Some of the mechanical and physical properties of this blend are given in Table I. This composition is an example of a polymeric donor–polymeric acceptor charge-transfer complex possessing usable mechanical properties, and as such, is the first representative of this class of materials.



I



II

R = bis(4,4′-oxyphenyl)-2, 2-propane

We prepared condensation polymers as donors since suitable choice of the functional groups therein should impart toughness. Previous work mainly utilized poly(vinyl aromatics). Polycarbonate I, containing the free tertiary amine group, was prepared in >95% yield by a low-temperature solution polycondensation between bisphenol A dichloroformate and *p*-anisyliminodiethanol. The latter compound was synthesized from *p*-anisidine and ethylene oxide. Since polyesters of isophthalic acid are known to be tough materials, we prepared a poly(mononitroisophthalate) for evaluation as one type of acceptor species. Reaction of 5-nitroisophthalic acid with ethylene oxide gives the requisite bis(hydroxyethyl ester) monomer.[6] This compound was polymerized with bisphenol A dichloroformate in the presence of pyridine to give the poly(ester carbonate) (II) in over 90% yield.

Other aspects of the synthesis and properties of this and other novel donor polymer–acceptor polymer charge-transfer systems will be reported in subsequent publications.

(6) Suitable elemental analyses were obtained by Galbraith Laboratories, Knoxville, Tenn.

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Some Unusual Properties of Poly(γ-benzyl L-glutamate) Films Cast in Strong Magnetic Fields

Poly(γ-benzyl L-glutamate) (PBLG) is known to have an α-helical molecular conformation in solution and in the solid state.[1,2] We present evidence for unusual supramolecular structures in cast films of PBLG, emphasizing the effect of magnetic fields. The nature of the cast films composed of these rodlike molecules is discussed in terms of (a) X-ray observations, (b) swelling characteristics of the films and (c) nmr of solvent molecules in the swollen film. The X-ray observations are correlated with the earlier work of Robinson, *et al.*, on the fluid liquid crystal phase of PBLG.[3] We observed the ability of concentrated solutions of this polypeptide to act as a liquid crystal solvent for nuclear magnetic resonance experiments as recently reported by other workers.[4,5]

Films of high molecular weight PBLG (Pilot Chemicals, lot G-98, mol wt, 275,000) 1 mm thick were prepared by slow evaporation of chloroform solutions.

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