

MULTICOMPONENT POLYMERS SYNTHESIZED BY FREE-RADICAL PROCESSES

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Abstract - This paper describes the requirements for free-radical reactions to be used in the synthesis of multi-component polymers of known structure. The principles of controlling the structures of graft-type copolymers (non-linear block copolymers) are reviewed in terms of results obtained with one type of initiating system. Selected data on morphologies and properties of polymers produced according to the guide-lines laid down are presented to illustrate types of material which are available by this route but not by other synthetic procedures. A new procedure which permits more detailed characterization of the polymers and provides a technique for studying the kinetics of graft polymerization is outlined.

INTRODUCTION

Following current practice we use the term multicomponent polymers to mean polymers prepared from more than one type of monomer unit in which like monomer units are attached in long sequences. Such materials include blends of homopolymers, certain types of copolymer and their blends with one or more homopolymers. Examples of the simplest and most relevant copolymer species in this category and based on two monomers A, B are depicted in Table 1, they include the linear AB and ABA block copolymers and non-linear block polymers

TABLE 1. Copolymer types

Designation	Monomer Sequence
AB block copolymer	-AAAAAABBBBB-
ABA block copolymer	-AAAABBB-BBBAAA-
AB graft copolymer (A <sub>2</sub> B block copolymer)	-----AAAAAA----- B B BBBB-----
AB crosslinked polymer (A <sub>2</sub> BA <sub>2</sub> block copolymer)	-----AAAAAA----- B B   B B -----AAAAAA-----

of graft and crosslinked types. The copolymers are normally prepared by sequential synthesis of the segments A and B and most commonly in that order.

The essential reason for widespread current interest in multicomponent polymers is the manner in which the properties of the final polymer reflect and combine the properties of the homopolymers of the constituents. The distinctive characteristics (e.g. two glass-transition temperatures) arise in consequence of the normal immiscibility of chemically different polymers, a phenomenon which gives rise to phase separation in homopolymer blends and microphase separation (due to segregation of the different constituents within the same molecule) in copolymers if the sequence lengths are sufficiently long.

The first reported synthesis of a block copolymer was a free-radical process involving trapped radicals (Ref.1). Subsequently a variety of processes were used to prepare block and graft copolymers (Refs. 2-7) and many of these processes involved free-radical reactions. However, it was not until after the development of anionic polymerization in the late 1950's (Refs. 8,9) and of poly(styrene-b-butadiene-b-styrene) triblock copolymers as thermoplastic elastomers in the 1960's (Ref. 10) that the scientific study of such materials became a topic of major interest.

Although Merrett (Ref. 11) recognised the occurrence of microphase separation in polymers formed by free-radical grafting of poly(methyl methacrylate) on to natural rubber the extensive consequences and implications of the phenomenon were not appreciated at that time. It was later, through the study of anionically prepared copolymers, that the phenomenon became well-known and that the fundamental morphologies were identified (Ref. 12). Subsequently, the connections between morphologies and properties became apparent.

Over the past fifteen years the anionic route to multicomponent copolymers has taken pride of place because it can be used to prepare very well-defined materials with narrow molecular-weight-distributions. Linear block copolymers prepared in this way are the most intensively investigated multicomponent polymers. In the same period free-radical reactions have come to be regarded as the Cinderella route to multicomponent polymers because the reaction products are less well-defined. This inferior position is somewhat unjustified because, although the products are less well-defined, free-radical routes do offer certain advantages. Not only do they permit a wider variety of components to be incorporated into copolymer structures but also allow the synthesis of structures which are not readily accessible by anionic polymerization.

While the commercialization of anionically prepared block copolymers proceeds steadily it is still true that the major tonnage application of multicomponent polymers is as impact-resistant plastics, prepared using radical reactions. These latter materials do not have well-characterized molecular structures but there is no reason why materials with defined structures, worthy of scientific investigation and of potential practical use can not be synthesized by free-radical polymerization. In this paper we consider the controlled synthesis of multicomponent polymers, briefly comment on morphologies and properties which can be obtained and describe a method of characterization which provides a means of investigating the detailed kinetics of graft polymerization.

#### CONTROLLED SYNTHESIS BY FREE-RADICAL REACTIONS

Whether radical reactions are used to prepare block or graft-type copolymers the products will almost inevitably be copolymer mixed with one or more homopolymers. The simplest situation that can be achieved is to prepare copolymer of known composition and structure mixed with known quantities of one homopolymer. To achieve this objective certain general requirements must be fulfilled and these may be simply stated as:

- (i) Preformed polymer (A) carrying reactive groups which can be used as reaction sites for radical formation (initiation);
- (ii) A highly specific radical forming process which ensures that all primary radicals are attached to A-chains;
- (iii) Homogeneous reaction conditions;
- (iv) Detailed control of the kinetics of polymerization of monomer B.

For the synthesis of non-linear copolymers a further condition is:

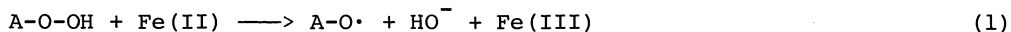
- (iv) Random bimolecular termination of B-chains.

There are obvious inter-relations between these conditions, for example (i) and (ii) together constitute a total initiating system. We shall consider how some of these aspects may be achieved.

#### Initiating systems

The prime requirement of an initiating system is to use reactive groups on preformed chains to generate radicals on those chains (macroradicals) only. Simple thermolysis or photolysis of an unstable group, such as peroxide, yields two radicals only one of which would be attached to the preformed polymer. The second radical would normally be free to initiate homopolymerization of monomer B. To avoid formation of the second radical it is necessary to generate radicals singly in a redox reaction.

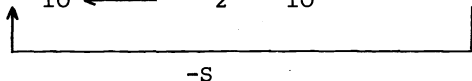
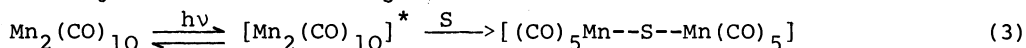
Hydroperoxide initiation. Probably the first potentially useful radical forming reaction for this purpose was the redox reaction between hydroperoxide and some suitable transition metal species, e.g. Fe(II), when reaction proceeds according to equation (1) (Ref. 13). The only radical formed and free



to initiate polymerization is A-O· and if A represents a preformed polymer chain the process fulfils requirements (i) and (ii). Unfortunately, there are complications in that the oxidised transition-metal species formed in (1), e.g. Fe(III), may terminate polymerization (Ref. 14) leading to kinetic complications.

Metal carbonyl + organic halide systems. Appropriately, within the context of this symposium, the method we use to synthesize multicomponent polymers evolved during collaborative studies with Professor Bamford's group into the mechanisms of new initiating systems and is based on the reactions between metal carbonyls and certain organic halides. Bamford and Finch (Ref. 15) identified some carbonyl-halide combinations which act as radical sources and derived relevant kinetic expressions; a summary of detailed mechanisms of radical formation is given elsewhere (Ref. 16). Complete initiation mechanisms are complex but it is necessary to establish them in detail to determine the rate laws for radical formation and initiation because, to prepare sufficient material for studies of mechanical properties, it is sometimes necessary to work under conditions of significant initiator consumption.

In every system the first and rate-determining step in the reaction mechanism is the formation of a reactive species from the metal carbonyl. Of the many combinations now investigated we usually use either thermal initiation at 80°C, using molybdenum carbonyl, or photoinitiation at 25°C ( $\lambda = 436\text{nm}$ ), using dimanganese decacarbonyl, and for these systems the first steps in the reaction mechanisms are given by equations (2), (3), respectively, in which S is a solvent and may be monomer. Equation (3) varies from the way in which



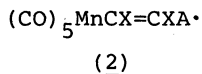
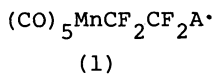
the initial step has been written previously to take account of recent data on quantum efficiencies of initiation in different monomers (Ref. 17) and known solvent effects (Ref. 18). Using isotopically labelled halides (carbon tetrachloride and ethyl trichloroacetate) we have demonstrated that in these particular systems radical formation occurs exclusively by abstraction of halogen from the halide R-Cl by the active species M(O) derived from the carbonyl in (2) or (3) according to equation (4) in which M(I)Cl represents an



oxidised metal species. Radical R· initiates polymerization if reaction is performed in a suitable monomer B. In the presence of halide concentrations greater than  $10^{-3} \text{ mol l}^{-1}$  (dependent on the carbonyl-halide combination) rates of radical formation are independent of [R-Cl].

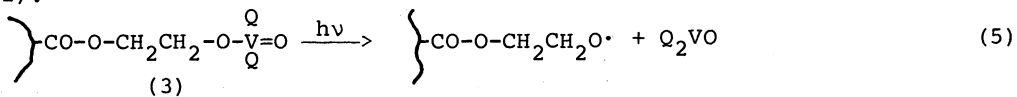
Reaction (4) also describes radical formation if the halogen is incorporated in reactive moieties in an A-polymer chain (i.e. if R = A) when the redox process generates a macroradical. Thus, these initiating systems fulfil the necessary requirements for synthesis of multicomponent polymers and we have employed them extensively.

Other metal carbonyl based systems. Professor Bamford's group has continued to investigate mechanisms of radical formation in organometallic systems and has identified a number of other systems which fulfil the requirements stated above. Amongst them are systems based on metal carbonyls and fluoro-olefins, e.g. photoinitiation by dimanganese decacarbonyl and tetrafluoroethylene. Initiation does not proceed by halogen atom abstraction from the fluoro-olefin but incorporates a manganese atom in the polymer chain. Bamford and Mullik proposed that in the presence of a monomer A initiation produces species (1) which becomes the terminal unit of a chain of polymer A (Ref. 19).



These workers also found that a similar reaction mechanism operates in photochemical reactions between certain metal carbonyls and substituted acetylenes ( $\text{XC}\equiv\text{CX}$ ) which incorporate species of structure (2) into polymer chains (Ref. 20). They further demonstrated that structures (1), (2) are thermally unstable and will initiate the polymerization of methyl methacrylate at  $100^\circ\text{C}$ ; they proposed that radical formation proceeds by scission of the Mn-C bond with loss of  $\text{Mn}(\text{CO})_5$  to form a radical capable of initiating polymerization (Ref. 21).

Metal chelates. Aliwi and Bamford studied the photolysis of vanadium chelates and demonstrated that alkoxy-oxobis(8-quinolyloxo)vanadium(V) chelates undergo photolysis ( $\lambda = 365\text{nm}$ ) to give alkoxy radicals capable of initiating polymerization of vinyl monomers. They incorporated the chelate function into side groups of polymer chains to give polymers of structure (3) which photolyse according to equation (5) ( $\text{Q} = 8\text{-quinolyloxo}$ ) to give a macroradical (Ref. 22).

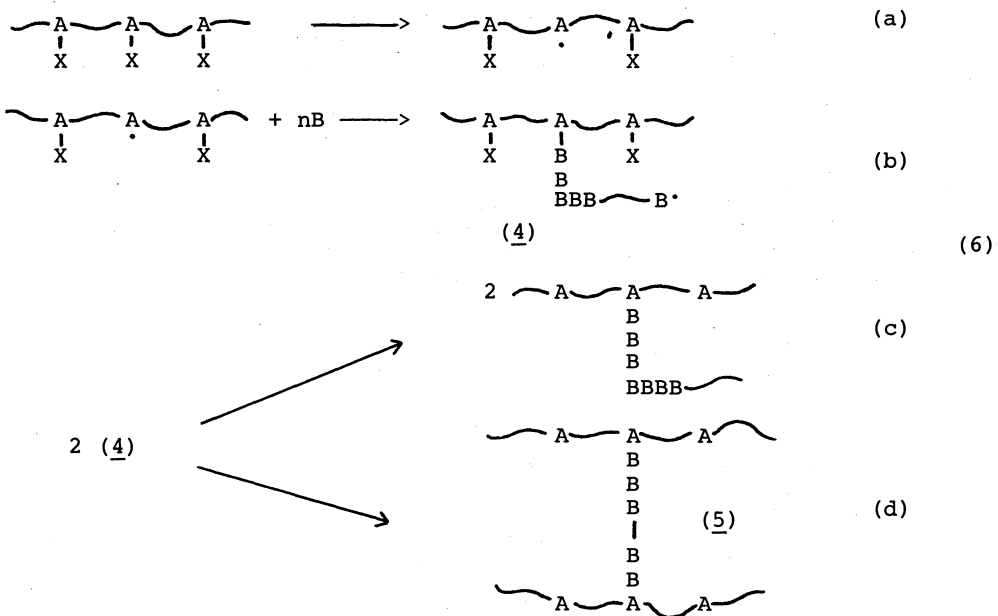


The feasibility of using the radical forming processes described in the last two sections to produce multicomponent polymers has been demonstrated but their potentialities have not yet been fully explored.

#### Preformed polymer

Given any suitable initiating system we can, in principle, use it to prepare linear or non-linear (graft) block copolymers. Reaction scheme (6) depicts the formation of non-linear species but an equivalent scheme can be written for synthesis of linear copolymers by using the reactive function (depicted as X) as the terminal unit of preformed A-chains. We have not exploited the synthesis of linear copolymers using the metal carbonyl - halide systems for practical reasons. To avoid kinetic complications it is advantageous to work with  $[\text{halide}] > 3 \times 10^{-3} \text{mol l}^{-1}$ . Assuming polymer A has a molecular weight in excess of  $20,000 \text{g mol}^{-1}$  (a typical value to ensure microphase separation in bulk polymer) the initial reaction mixture should contain at least 6% (w/v) of polymer A in solution of monomer B. Such conditions will certainly sustain reaction but are not the most suitable for control of the kinetics of polymerization of monomer B; systems of high viscosity will be generated and compositions of the solutions may not remain uniform as the total polymer content increases to 10-20% (w/v) as monomer B polymerizes.

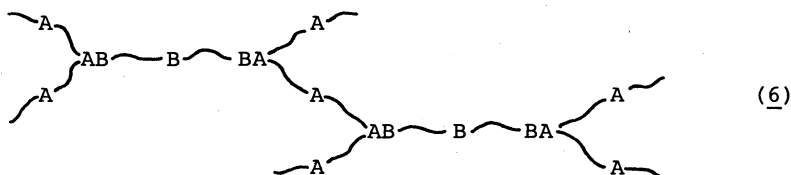
We have concentrated the synthesis of non-linear block copolymers because if the molecular weights and functionality of the A-chains are high (say, one hundred or more) then relatively high base molar concentrations of prepolymer can be achieved at modest concentrations (1-2% (w/v)) of polymer A in monomer B. Then copolymer formation proceeds according to scheme (6), where groups X are moieties containing reactive halogen. Radical formation occurs through reaction of a group X with an active species derived from the carbonyl in (6a) in an analogous manner to reaction (4). Then, in (6b) the radical initiates the polymerization of monomer B to produce a propagating graft. Disproportionation termination of the growing grafts yield graft copolymer in (6c) and combination termination yields AB crosslinked polymer in (6d);



unreacted groups X are not shown for clarity.

In early studies we used poly(vinyl trichloroacetate) as polymer A and more recently have made extensive use of the polycarbonate prepared by condensing 1,1,1-trichloro-bis-2-(p-hydroxyphenyl)ethane with phosgene. Very recently we have used N-chloronylon-66.

Let us restrict our attention to systems in which propagating B-chains undergo termination exclusively by radical combination; i.e. (6c) does not occur. Initiation is a slow process and steadily forms radicals at random sites on A-chains throughout the course of the reaction. In the earliest stages the polymeric species in the reaction mixture consist predominantly of unreacted A-chains together with a few species of structure (5). As reaction proceeds more A-chains will be involved and produce more of these simple species. However, because of the high functionality of the A-chains, reaction will take place at additional sites on A-chains already in multicomponent species to produce more complex species, such as (6), and, gradually, more complex structures. At some stage the reaction mixture gels as infinite network



structures are generated. By stopping reaction prior to gelation the product of reaction is a mixture of relatively simple species which are soluble and can be solvent-cast into films.

Using solvent-cast films we can study the morphologies and properties of the multicomponent polymers. For detailed studies and to interpret the morphologies and properties in terms of molecular structures we need to define:

- (i) reaction conditions which permit control over the molecular species formed
- (ii) the populations of different species
- (iii) the detailed structures of multicomponent species, e.g. molecular weights of B-chains.

## RANDOM INTRODUCTION OF B-CHAINS

Formation of multicomponent species by the procedure outlined above is in effect the introduction of B-crosslinks into an assembly of A-chains. Formally, this is the same as any other crosslinking reaction except that in our case the crosslinks are high-molecular-weight chains rather than short linkages introduced by, say, a vulcanization process. To determine the structures of species generated and their populations it is necessary to introduce the B-chains randomly between A-chains. Essentially all B-chains must act as intermolecular crosslinks between different A-chains which should not be otherwise attached within the same molecular structure. Radical formation will occur essentially at random and, therefore, random crosslinking requires random termination of propagating B-grafts.

Random crosslinking will result in a family of multicomponent species being formed which consist of  $n$  A-chains and  $n-1$  B-chains. The object of the exercise, therefore, is to define the populations of species with different values of  $n$ . Deviations from random crosslinking result in intramolecular crosslinking when the structures produced and their populations become undefinable. Even estimates of the extent of intramolecular crosslinking can only be made by comparison with data obtained under conditions of random crosslinking. It is, therefore, necessary to define reaction conditions for random crosslinking.

Gelation Theory

Following gelation theory developed by Flory (Ref. 23) and Stockmayer (Ref. 24) we derived (Ref. 25) the equation

$$t_g = c/\bar{P}_w \mathcal{f} \quad (7)$$

which defines the time to reach the critical condition for gelation (gel time)  $t_g$  for random crosslinking of an assembly of preformed chains (A-chains). In equation (7)  $c$  is the base molar concentration of potential crosslinking junction points (halogen-containing groups),  $\bar{P}_w$  is the weight-average degree of polymerization of those groups and  $\mathcal{f}$  is the rate at which they are incorporated into crosslinks (i.e. the rate of initiation of B-chains). Simple modifications can be applied to equation (7) to allow for disproportionation termination, initiator consumption and/or chain transfer (Ref. 18).

Gelation kinetics

For equation (7) to apply in a practical situation requires that all crosslinking is intermolecular. Any intramolecular crosslinking will increase the observed gel time  $t_{g,obs}$  which may then be described by equation (8) where  $k$  is some correction factor ( $k > 1$ ).

$$t_{g,obs} = kc/\bar{P}_w \mathcal{f} \quad (8)$$

In our early studies we established reaction conditions under which the proportionalities between  $t_g$  and  $c$  and the reciprocal of  $\mathcal{f}$  hold simultaneously (Ref. 25). These conditions are essentially high  $c$  (typically  $c > 5 \times 10^{-3}$  b. mol  $l^{-1}$ ) and low  $\mathcal{f}$  (typically  $\mathcal{f} < 3 \times 10^{-7}$  mol  $l^{-1}$  s $^{-1}$ ); limits on  $c$  and  $\mathcal{f}$  vary according to the initiating system in use. Recently we have shown that under conditions where the above proportionalities hold  $t_g$  is also proportional to  $1/\bar{P}_w$  (Ref. 17).

We have previously suggested that long gel times, e.g. at high  $\mathcal{f}$ , are, at least in part, a consequence of having two active propagating B-chains attached simultaneously to one A-chain and an enhanced rate of termination between such chains (Ref. 25).

Recent data (Ref. 17) indicate that under conditions where the proportionalities indicated in (8) apply  $k$  does not exceed 1.1. This factor may reflect the inevitability of a limited amount of intramolecular crosslinking. The probability of such reactions will increase as the gel point is approached when more complex species are present. It, therefore, seems reasonable to assume that, under conditions where the above proportionalities apply, intramolecular crosslinking may be neglected in the early stages of reaction.

Populations of species

Having established reaction conditions under which random crosslinking is approximated to, we can attempt to define the populations of various species present as a function of the extent of crosslinking. A parameter which has been used to quantify the extent of crosslinking is the crosslinking index,

defined as the number of crosslinked units per primary molecule (Ref. 26). For A-chains homogeneous in molecular weight the critical conditions for gelation is a crosslinking index of unity. For A-chains with an arbitrary molecular weight distribution the critical condition for gelation is one crosslinked unit per weight average A-chain (Ref. 24) and the critical value of the crosslinking index depends on the shape of the distribution of molecular weights of A-chains. As a practical convenience we have defined a relative crosslinking index  $\gamma_r$  as the number of crosslinked units per weight average A-chain (Ref. 27) so that  $\gamma_r$  is proportional to the number of B-chains in the system and is unity at the gel point.

Flory calculated the weight fractions of species containing different numbers of chains as a function of the extent of crosslinking in a simple crosslinking polycondensation (Ref. 23). Stockmayer extended these calculations and derived equations for the weight fractions of species containing  $n$  primary chains for random crosslinking of an assembly of primary chains with an arbitrary molecular weight distribution (Ref. 24).

We have recently applied Stockmayer's equations to a system relevant to the synthesis of multicomponent polymers, i.e. to the crosslinking of a preformed polymer prepared by condensation polymerization; this situation relates to crosslinking polycarbonate A-chains (Ref. 28). Our calculations are still incomplete but preliminary results show that prior to gelation the populations of species of different complexity vary according to the pattern obtained for crosslinking polycondensations. Some of our results are presented in Table 2 which presents weight fractions of polymer A in species containing 1 (homopolymer), 2 and 3 A-chains for selected values of  $\gamma_r$ . From the data in

TABLE 2. Weight fractions of all A-chains in species containing  $n$  A-chains present after crosslinking to different relative crosslinking indices  $\gamma_r$ .

$\gamma_r$	Weight fractions of A-chains, $w_n$			
	$n = 1$	$n = 2$	$n = 3$	$\sum_{n=1}^{n=3} w_n$
0.2	0.818	0.128	0.033	0.977
0.3			0.054	
0.4	0.686	0.168	0.069	0.923
0.5			0.080	
0.6	0.583	0.172	0.085	0.840
0.8	0.500	0.160	0.086	0.746
1.0	0.434	0.144		

Calculation assumed primary A-chains have a molecular weight distribution corresponding to that of a polymer produced by condensation polymerization to an extent of reaction of 0.9.

Table 2 it is apparent that the weight fraction of unreacted A-chains ( $n=1$ ) decreases monotonically. The weight fractions of A-chains in species with  $n=2$  ( $A_2BA_2$  block copolymer) increases to a maximum and then decreases as these species are built into more complex structures. Species with  $n=2$  are, of course, being generated continuously but their rate of removal into complex species increases as  $\gamma_r$  increases. More slowly, in the initial stages, complex species (e.g.  $n=3$ ) build up but, as found by Flory, the weight fractions of species always decreases as their complexity increases. Only when  $\gamma_r$  exceeds 0.4 does the total weight fraction of A-chains in relatively simple species depart significantly from unity as more-complex species ( $n>3$ ) are generated. However, the number fraction of such complex species is not great since predictions from computer-simulated crosslinking experiments confirm the intuitive expectation that the longer primary A-chains are

preferentially incorporated into complex species because of their higher functionality.

Considerations as outlined above predict that in the grafting (crosslinking) reactions we employ, especially at low degrees of grafting, the reaction products comprise a mixture of A-homopolymer and relatively simple multi-component species. Also, in those multicomponent species the average number of B-chains attached to any reacted A-chain is only a little greater than unity. We suggest, therefore, that we are justified in considering the products of controlled grafting and crosslinking reactions to be blends of homopolymer A and simple non-linear block copolymers. Using such reaction conditions we have prepared a variety of multicomponent polymers for investigation.

#### MORPHOLOGIES AND PROPERTIES

Our more recent studies of multicomponent polymers have been restricted to lightly crosslinked materials such that considerations of the preceding sections are justifiable. Polymers have been carefully solvent-cast from homogeneous solution into films approximately 0.25mm thick. For materials in which the B-chains terminate exclusively by radical combination (e.g. styrene and chloroprene) we assume, for simplicity of discussion, that the polymers under investigation are blends of  $A_2BA_2$  block copolymer with A-homopolymer.

##### Polymer morphologies

Electron microscope studies of pure anionically-prepared AB and ABA block copolymers have previously established the existence of certain fundamental morphologies which arise as a result of microphase separation of the blocks of A- and B-components (Ref. 12). These morphologies are spheres or cylinders of the minor component in a matrix of the other or alternating A, B lamellae. The equilibrium morphology for a polymer is determined by the relative volume fractions of A- and B-components and varies through the sequence A-spheres, A-cylinders, lamellae, B-cylinders, B-spheres as the composition changes from a very small to a very large A-content. Theoretical studies have explained the origins of these morphologies in terms of the relative magnitudes of the A- and B-blocks and have predicted relations between the characteristic dimensions of the microphases and the molecular weights of the constituent blocks (Refs. 29-31).

Our studies, using electron microscopy of ultra-thin sections, have revealed the existence of the same basic morphologies in AB-crosslinked polymers as observed in pure linear block copolymers. In these materials the morphology adopted is not determined by the copolymer structure alone but, to a large extent, by the overall composition (Refs. 32, 33). Some of the materials we have investigated undergo macroscopic phase separation into copolymer-rich and homopolymer-rich phases and give seemingly complex morphologies as a consequence of formation of different standard morphologies within restricted volume elements (Refs. 33,34). Although phase separation provides a closer approximation to the equilibrium situation for many of the homopolymer/copolymer blends under investigation, subsequent comments in this section refer primarily to materials cast under conditions which give a uniform morphology throughout the sample. Nevertheless, the comments do have relevance to the local morphologies which result from microphase separation in each of the phases produced by true phase separation.

Materials in which the B-chains are short compared with the A-chains or when  $\gamma_r$  is low (i.e. materials in which A is by far the major component) exhibit a morphology of spherical domains of polymer B dispersed throughout a matrix of A, Fig. 1(a). Because of the presence of A-homopolymer interdomain distances are not determined by A-chain dimensions and domain packing is not as regular as normally observed in pure linear block copolymers. In spite of the presence of A-homopolymer, if the volume fractions of A- and B-components are comparable careful sample preparation can result in a material having a regular lamellar morphology with a considerable degree of long-range order, Fig. 1(b).

Knowing that the AB-crosslinked polymers we are dealing with are on assembly of simple molecular structures it is not surprising that microphase separation occurs as in linear block copolymers; Fig. 2 is a schematic representation of spherical or cylindrical microphases of component B in an A-matrix of AB and  $A_2BA_2$  block copolymers. Nor is it surprising that the same general



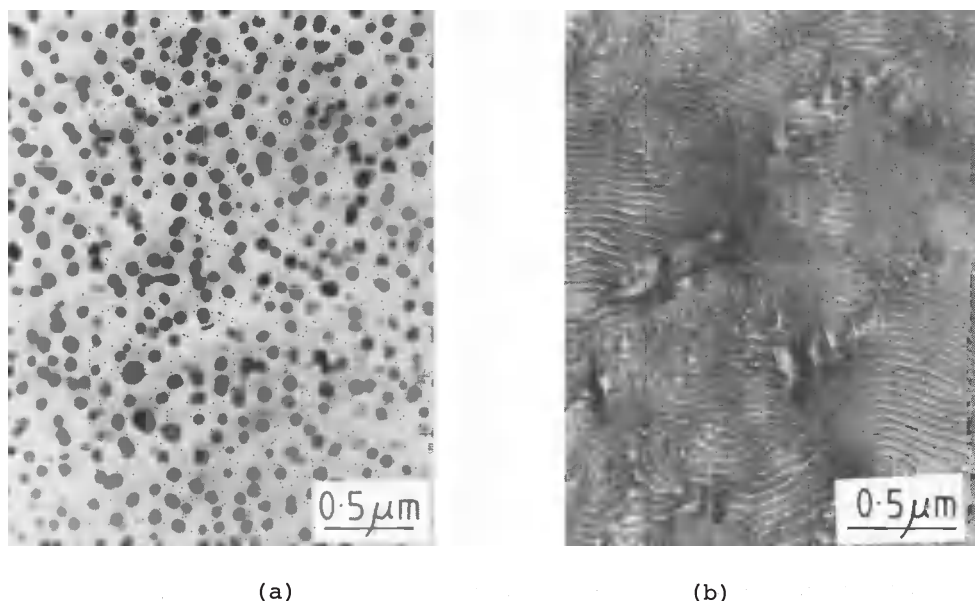


Fig. 1. Electron micrographs of (a) polystyrene ( $\bar{M}_n = 124 \text{ kg mol}^{-1}$ ) crosslinked with polychloroprene ( $\bar{M}_n = 522 \text{ kg mol}^{-1}$ ) to  $\gamma_r = 0.83$ , stained with osmium tetroxide (polychloroprene appears dark); (b) polycarbonate ( $\bar{M}_n = 16 \text{ kg mol}^{-1}$ ) crosslinked with polystyrene ( $\bar{M}_n = 96 \text{ kg mol}^{-1}$ ) to  $\gamma_r = 0.35$ , unstained (polycarbonate appears dark).

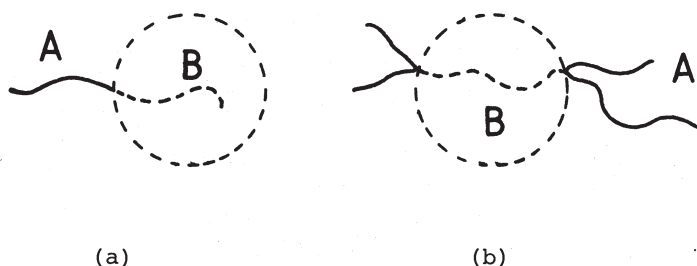


Fig. 2. Schematic representation of microphase separation in (a) AB; (b)  $A_2BA_2$  block copolymers.

morphologies are observed. When a polymer undergoes microphase separation the driving force is the formation of like-like polymer contacts in preference to like-unlike. The immediate consequence of microphase separation is the generation of an interface between the A- and B-components. Introduction of the interface imposes severe constraints on the location of the chain segments and the coiling of the chains. Assuming that energy terms associated with the generation of the interface are unfavourable and that these factors play a major role in controlling polymer morphology the system will try to minimise the interfacial area. Then, following the arguments of Berthold and Errera, we should expect to find only those morphologies actually observed (Ref. 35); such generalised considerations require no knowledge of the molecular structures involved. We might anticipate that in copolymer systems molecular structures will have a role in determining the morphologies, most probably in determining the compositions which define the boundaries between the different morphologies in particular systems.

Detailed examination of micrographs of AB-crosslinked polymers having a morphology of spherical B-domains reveals certain general features (Ref. 32). First, although the B-chains have a broader distribution of molecular weights than do anionically prepared polymers the distribution of domain diameters is, nevertheless, fairly narrow. Second, for chains of a given molecular weight diameters of B-domains in AB-crosslinked polymers are much smaller than (about 1/3) would be expected in ABA block copolymers. The first of these observations implies no fractionation of B-chains on microphase separation. We

proposed an explanation of the second observation in terms of chain packing in the vicinity of the interface. A major distinction between linear and non-linear species is the relative numbers of chains on each side of the interface; in linear systems they are equal and are unequal in non-linear systems, see Fig. 2. We suggested that two A-chains attached to a single junction point at the interface occupy a greater effective area than would one A-chain of the same total molecular weight as the two chains. We argued that, on packing considerations alone, this effect would reduce the radius of curvature of the domains, resulting in smaller domains containing fewer B-chains than in a linear block copolymer with comparable B-chains.

While the above observations certainly have implications with regard to the coiling and conformations of chains in domains, factors such as a tendency to reduce radii of curvature have implications with regard to the polymer compositions which define the boundaries between different morphologies. An additional factor in this latter regard and one which must be taken into account in a generalised theory of polymer morphology is the consequence of the presence of any homopolymer (polymer A the present case) and the relative molecular weights of A-chains in homopolymer and copolymer.

#### Mechanical properties

Since we are able to prepare multicomponent polymers with well-defined and fairly uniform morphologies we have undertaken an investigation of the physical and mechanical properties of these materials. Here we describe very briefly examples of the mechanical properties of some polymers taken from our recent studies to illustrate the types of behaviour which can be obtained with free-radically prepared polymers (Refs. 28,36,37); more comprehensive and detailed accounts of these data will be presented elsewhere.

Stress-strain data were obtained using standard dumb-bell shaped samples cut from carefully-dried solvent-cast films. Curve (a) in Fig. 3 is a stress-strain curve for a polycarbonate copolymer ( $\bar{M}_n = 15 \text{ kg mol}^{-1}$ ) prepared from a 50:50 molar mixture of bisphenol-A and 1,1,1-trichloro-bis-2-(*p*-hydroxyphenyl) ethane and shows very similar behaviour to that of conventional polycarbonate.

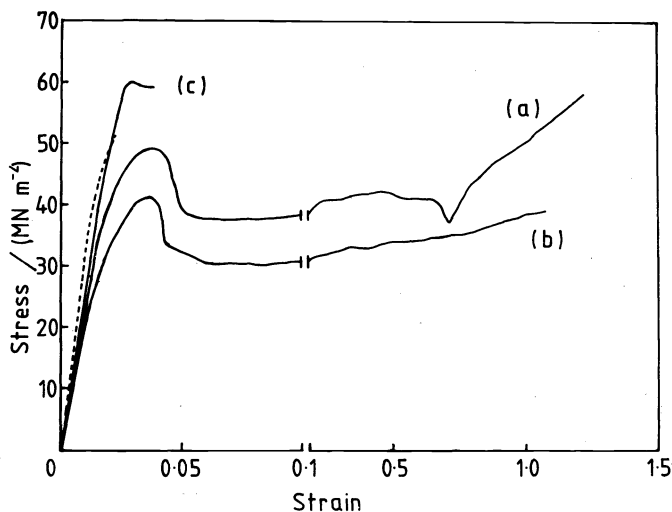


Fig. 3. Stress-strain curves for polymers described in text, dotted line refers to polystyrene and is based on literature data. Note change in scale at strain = 0.1.

Polycarbonate-polychloroprene combinations. Curve (b) in Fig. 3 relates to the above polycarbonate (PCarb) crosslinked with polychloroprene ( $\bar{M}_n = 23.1 \text{ kg mol}^{-1}$ ) to  $\gamma_r = 0.55$ , the sample contained 16% (w/w) polychloroprene. Comparison of curves (a), (b) reveals that the copolymer has a slightly lower modulus and lower yield and ultimate strengths than the PCarb. These features are common to other work where a rubber component is incorporated into a high-modulus matrix. The only distinction from other studies is that the extension to break is not increased but PCarb itself has a large extension to break whereas polystyrene (a common matrix material) fails at very low strain

( $\sim 0.02$ ).

Inclusion of sufficient polychloroprene to give a polychloroprene matrix results in the formation of an elastomeric material, capable of considerable extension to break, having a low initial modulus and exhibiting strain hardening at high extensions (Ref. 36).

**Polycarbonate-polystyrene combinations.** Several materials have been prepared by crosslinking polycarbonate with polystyrene (PSt) and curve (c) in Fig. 3 relates to a sample with long PSt crosslinks ( $M_n \sim 257 \text{ kg mol}^{-1}$ ;  $\gamma_r = 0.7$ ; 75% (w/w) PSt); also shown is a typical stress-strain curve for PSt derived from literature data (Ref. 38). The copolymer has a morphology of dispersed PCarb spheres in a PSt matrix and is, in effect, a plastic-filled plastic. Comparison of the curves reveals that, as expected, the modulus of the composite lies between those of the homopolymers of the constituents. Of more interest and significance is the fact that inclusion of 25% (w/w) PCarb into a PSt matrix has, compared with the properties of PSt, increased the extension to break and the ultimate strength and has introduced a yielding process. Thus, introduction of PCarb has to some extent toughened the PSt without causing a significant decrease in modulus such as accompanies rubber-toughening (Refs. 28,36).

This PCarb/PSt polymer has other interesting properties. Because it has a PSt matrix it becomes elastomeric at temperatures above  $100^\circ\text{C}$  and is a low-modulus rubber at  $140^\circ\text{C}$ . As an elastomer it has high extensibility ( $>700\%$  without fracture) and rapid 100% recovery. Not surprising, on reflection, it behaves at elevated temperature in a manner similar to conventional thermo-plastic elastomers at room temperature but has a high upper working temperature in consequence of the high PCarb glass-transition temperature ( $\sim 200^\circ\text{C}$ ). In addition the polymer may be strain-orientated when hot to produce a polymer with excellent unidirectional properties at room temperature and with potentiality as a novel heat-shrink plastic.

Very recently we have extended our studies into the dynamic-mechanical properties of multicomponent polymers. Figure 4 shows variations in real ( $E'$ ) and imaginary ( $E''$ ) moduli with temperature for PSt, PCarb and the PCarb/PSt

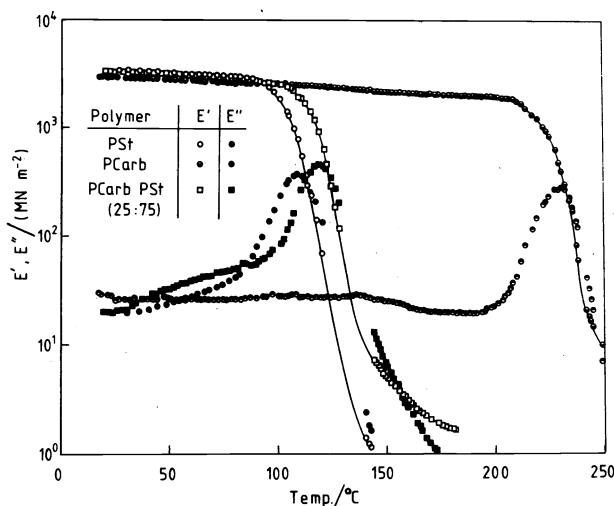


Fig. 4. Variations in real ( $E'$ ) and imaginary ( $E''$ ) tensile moduli of polymers described in text.

copolymer just described; data were obtained using a Rheovibron operating at 110 Hz. The most obvious feature which emerges from these data is that the copolymer has a major relaxation associated with the PSt matrix and this relaxation occurs at a higher temperature than in the PSt homopolymer. The  $\alpha$ -relaxation for the PCarb is not observable in this sample but can be seen in other samples with a higher PCarb content when that relaxation occurs at essentially the same temperature as in the PCarb (Ref. 37). Measurements at different frequencies show that the activation energy for the matrix in the

PCarb/PSt copolymer is higher ( $120 \text{ kcal mol}^{-1}$ ) than in pure PSt homopolymer ( $80 \text{ kcal mol}^{-1}$ ).

We believe that the elevated transition temperature for the PSt matrix and high activation energy are a consequence of incomplete microphase separation and incorporation of some PCarb in the PSt matrix. In agreement with this view is the observation that detailed behaviour is dependent on solvent-casting conditions (Ref. 37). Probably, the element of toughening described above is also a consequence of incomplete microphase separation.

The limited examples of properties described suffice to demonstrate that the general features of the mechanical properties of free-radically prepared multicomponent polymers are understandable in terms of the properties of anionically prepared materials. The materials described here do not have real counterparts prepared by other techniques and provide an interesting extension to materials currently available for investigation.

#### CHARACTERIZATION OF COPOLYMER STRUCTURE

Although we now have an appreciation of the general structural features of the copolymer species in AB-crosslinked polymers, to justify a detailed investigation of their physical and mechanical properties we require an even better understanding of detailed structure. Only then will it be possible to have confidence in relations between properties and molecular structure. The major parameter about which it is necessary to have more detailed knowledge is the molecular weight of the B-chains.

Previously we have noted that before gelation the kinetics of polymerization of the B-monomer are 'near normal'. In the absence of better information we have indeed assumed that the kinetics of graft polymerization are normal and have calculated the molecular weights of the B-chains accordingly. We have now developed a method of obtaining additional information (Ref. 17). This involves crosslinking PCarb with, say, PSt, then degrading the PCarb, isolating the PSt crosslinks and determining their molecular weight and molecular-weight distribution.

Recently we carried out the above exercise on a number of PCarb/PSt materials prepared under conditions of essentially random crosslinking and also under conditions which deviate from random crosslinking. We shall restrict our attention to two examples; further examples and more comprehensive discussion will be presented elsewhere.

##### Random crosslinking

First, we consider a situation in which the conditions for random crosslinking, discussed earlier, apply. Figure 5(a) shows conversion time curves, prior to gelation, for the homopolymerization of styrene and for the graft polymerization of styrene from a PCarb backbone at the same rates of initiation (using photoinitiation with dimanganese decacarbonyl). From these data it is seen that the rate of graft polymerization is somewhat greater than that for homopolymerization. These rate data correlate with the molecular-weight distributions (weight-fraction distributions) derived from gel permeation chromatograms of PSt crosslinks (formed by crosslinking PCarb to  $\gamma_r = 0.76$ ) and PSt homopolymer prepared under the reaction conditions used to obtain the rate data and for a similar reaction time; the molecular weight distributions are normalised; see Fig. 5(b).

The peak molecular weights of the two distributions are virtually identical but the average molecular weight of the crosslinks is slightly higher than the PSt homopolymer. The difference arises as a result of smaller weight fractions at low molecular weight in the crosslinks and slightly higher weight fractions extending to high molecular weights. Thus, on average the styrene grafts, which form the crosslinks, grow longer than homopolymer chains, an effect consistent with the higher rate of graft polymerization. There is no reason to assume the rate coefficient for propagation of the grafts is higher than that for homopolymerization and we attribute the effects to a lower value of the rate coefficient for termination  $k_t$  for propagating grafts than for free chains.

We suggest two reasons for a low value of  $k_t$  for grafts which are a consequence of the B-grafts being attached to A-chains. We previously suggested that the translational diffusion of radicals attached to A-chains would be impeded with respect to unattached chains and that this could result in a

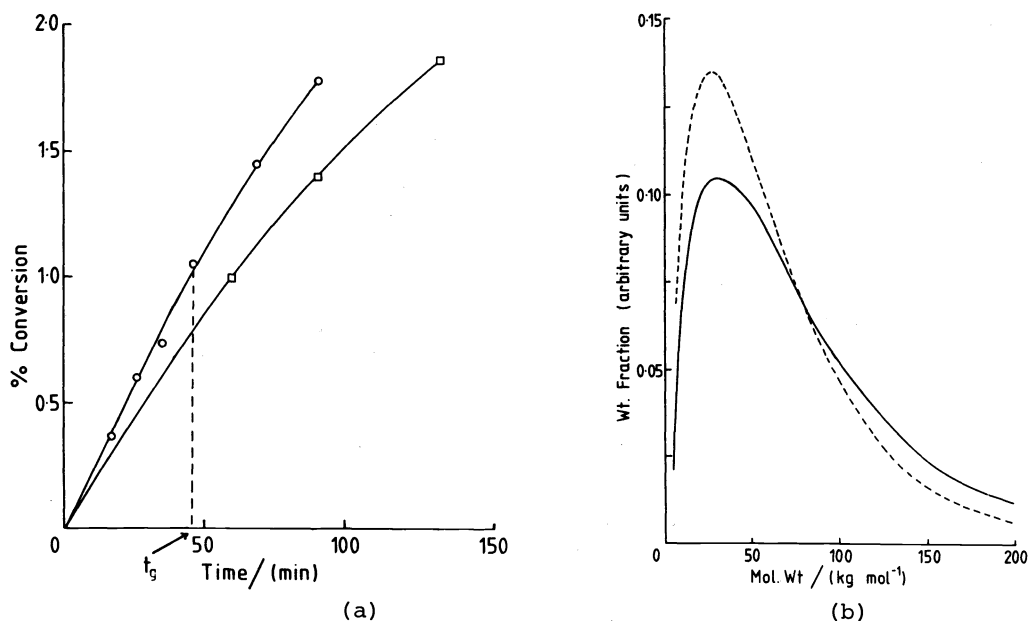


Fig. 5. (a) Conversion-time curves for homopolymerization of styrene ( $\square$ ) and graft-polymerization of styrene from polycarbonate ( $\bar{M}_w = 46.3 \text{ kg mol}^{-1}$ ) ( $\circ$ ); at the same rates of initiation. (b) Molecular-weight distributions of polystyrene chains produced by (—) graft polymerization (to  $\gamma_r = 0.76$ ) and (---) homopolymerization. Reaction conditions approximate to those for random crosslinking.

reduction in  $k_t$  (Ref. 25). This effect is consistent with the views of Mahabadi and O'Driscoll who have proposed that  $k_t$  decreases with increasing chain length, especially for short chains (Ref. 39); see also paper in this symposium. In a normal free-radical homopolymerization many acts of termination involve short chain radicals. However, in a graft polymerization short grafts are attached to A-chains, predominantly long A-chains, and their diffusion will be restricted. Consequently, compared with a simple homopolymerization the average value of  $k_t$  in a grafting reaction will be reduced and chains will grow longer.

In addition, propagating B-grafts will often form in the interior of coils of A-chains, in regions of high concentration of A-segments. As propagation proceeds and the B-chain grows, its inherent immiscibility with A-chains will cause the A- and B-components to segregate and the B-radical to be located in a B-rich environment. Termination of this radical with a short radical in an A-rich environment will obviously be unlikely and the probable consequence will be a further reduction in  $k_t$ .

#### Non-random termination

As a second example we consider polymerizations conducted under high rates of initiation where equation (8) does not hold; gel times are longer than anticipated. We previously attributed this effect to excessive intramolecular crosslinking resulting from a high probability of having two propagating B-chains simultaneously attached to one A-chain (Ref. 25).

In the particular example chosen to illustrate this situation rates of homopolymerization and graft polymerization are virtually identical (Fig. 6(a)). However, the similarity in rates is coincidental. Figure 6(b) shows molecular weight distributions for PST crosslinks and homopolymer prepared under the conditions relating to Fig. 6(a), reaction time corresponding to  $\gamma_r = 0.6$ . Comparison of the molecular weight distributions shows that the peak of the distribution for the crosslinks is at lower molecular weight than for the homopolymer. The weight fractions for the crosslinks are higher than for homopolymer chains at very low and high molecular weights and lower at intermediate molecular weights. Thus, in the grafting polymerization some chains grow shorter and some longer than they would in a normal polymerization. The two effects happen to compensate and give virtually identical rates of polymerization in this case. The increased weight fractions at high molecular weight we attribute to effects described in the preceding section and the

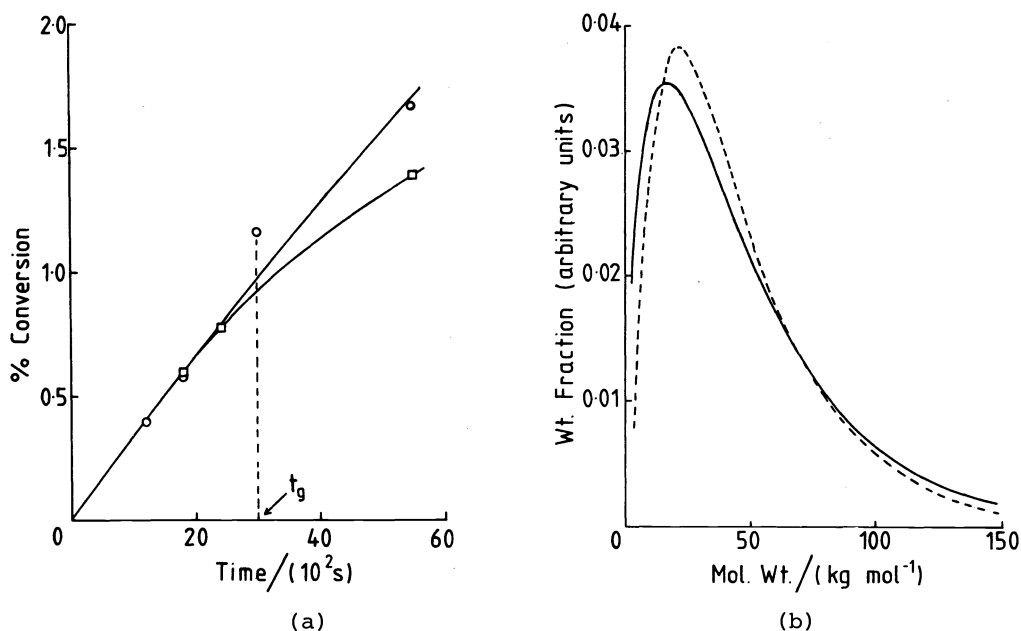


Fig. 6. (a) Conversion-time curves for homopolymerization of styrene ( $\square$ ) and graft-polymerization of styrene from polycarbonate ( $M_w = 46.3 \text{ kg mol}^{-1}$ ) (O); at the same (high) rates of initiation. (b) Molecular-weight distributions of polystyrene chains produced by (—) graft polymerization (to  $\gamma_r = 0.6$ ) and (---) homopolymerization. Reaction conditions deviate from those of random crosslinking.

high weight fractions at low molecular weight to enhanced intramolecular crosslinking. To this latter effect we attribute a high value of  $k_t$ .

#### SUMMARY

In this paper we have reviewed how, by use of specialised initiating systems, a method has been developed for the synthesis of multicomponent polymers, specifically graft-type copolymers, by free-radical routes. By controlling the kinetics of the free-radical polymerizations polymers of controlled structure can be prepared. This procedure can and has now been used to synthesise some novel copolymers which are unavailable by other routes. The results described demonstrate how the investigation of such polymers can extend the understanding of multicomponent polymers in general and raises questions with regard to the extension of concepts developed for simpler materials. By using a recently developed procedure we are now able to characterize the multicomponent polymers more completely than has hitherto been possible. This development provides a tool which will facilitate the detailed study of graft polymerization kinetics and will also provide a more accurate description of the molecular structure of the polymers under investigation. This latter aspect is especially important in attempts to relate morphologies and properties to molecular structures.

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