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Review

Chain Folding in Lamellar Crystals

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ABSTRACT: Small-angle neutron scattering yields a gyration radius and a segment distribution of the linear polyethylene molecule which can be best interpreted by a model based on the original suggestion by Frank and the analysis by Flory of chain folding on the boundary between the crystal core and the amorphous surface layer. In order to provide space for the amorphous chains half the stems in the crystal lattice must be connected by regular loops with adjacent reentry. One third of all the stems must be connected by random loops in order to reproduce the small-angle neutron-scattering data on samples quenched from the melt.

Orientation of long macromolecules (about 200 nm and longer) in a very thin polymer crystal (about 20 nm) permits only accommodation of a very short section of the chain in one single passage through the lamella. At the surface of the lamella the chain must either fold back, go into another crystal, or form a cilium, i.e., remain in the amorphous surface layer. Folding at the lamella surface involves either adjacent or random reentry. The fold itself is either taut, i.e., regular, or loose, i.e., substantially longer than the distance between the exit and the reentry of the chain into the crystalline matrix.

In the case of random reentry one generally assumes that the extended loop length is much larger than the end-to-end distance between the fixation points of the loop in the crystal. In the case of adjacent reentry, however, some loops can be regular and some are loose. The loose loops with adjacent or random reentry comprise the amorphous surface layers on both sides of the lamella. The regular loops of linear polyethylene (LPE) with a high concentration of gauche conformations increase the surface tension.[1] No such increase is derivable for loose loops, but the free energy of the amorphous layer on the fold surface is so much higher than that of the crystal that it may be sufficient for the explanation of the observed difference between the surface tension on the fold surface and that on the side faces of the lamella.

In single crystals obtained from dilute solution one can make the extreme assumption that all the folds are regular with adjacent reentry. The only contribution to an eventual amorphous layer on the fold-containing surfaces of the lamella comes from the free chain ends (cilia) or adsorbed macromolecules. If the folds are not regular or if at least some random reentry is permitted the surface layer also contains loose loops with adjacent or random reentry. The other extreme case would have all the loops loose and all the reentries at random without any adjacent reentry.

In crystallization from the melt or from a concentrated solution one knows that the crystal lattice of any lamella is separated from that of the next parallel lamella by an amorphous layer. It contains loose loops with adjacent or random reentry, cilia, and tie molecules, i.e., molecules which instead of reentering the same crystal extend from one crystal to the next one. If every crystal stem is connected through tie molecules to a stem in the adjacent lamellae, one has a typical fringed micelle model.

So far one has not had any convincing experimental method for deciding about the correctness of such a model. One has been mainly compelled to consider the compatibility of models with different properties of crystalline polymers which may be affected by both the kind of loops and the probability of chains extending from one lamella to another. No clear-cut answer could be derived from the data although on very general grounds one could exclude some extreme cases. Even with the small-angle-scattering experiments involving slow neutrons which were performed in the last few years one is not substantially better off, although the purely geometrical information they supply about average dimensions and spatial distribution of chain sections leaves less latitude for speculation than was the case with older methods. But a reasonable compromise between the above extreme cases based on neutron scattering explains the experimental facts with less effort than

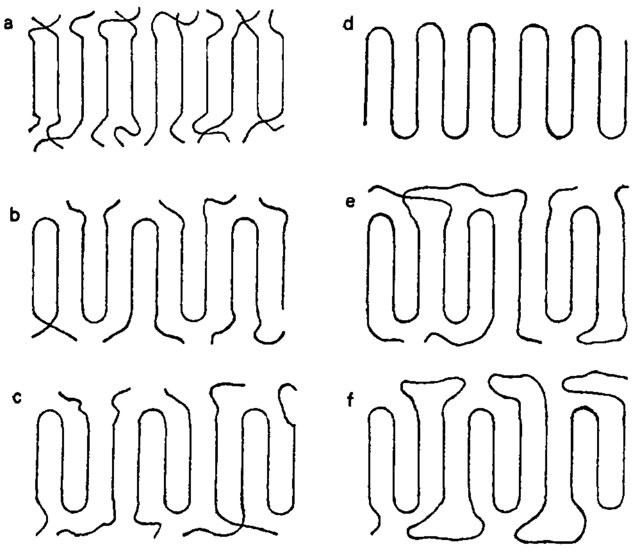

Figure 1. Models of chain folding: (a) Fringed micelle model with each stem in the crystal lattice continuing on both sides as a tie molecule with a random conformation. The resulting density $\rho_a > \rho_c$. (b and c) A simplified Flory model with at least half the stems connected by regular loops with adjacent reentry. The rest of the loops are loose with either adjacent or random reentry. The regular loops alternate on both sides of the crystal core (b) or are shifted to one side by one stem (c). The resulting density $\rho_a < \rho_c$. (d) All loops are regular with adjacent reentry. No amorphous layer is possible. This requires a hollow pyramid habit of the single crystals. (e) On the average three adjacent stems connected by two regular loops with adjacent reentry belong to the same molecule. A perfectly loose loop connects two consecutive clusters of the same molecule. The resulting density $\rho_a < \rho_c$. (f) All loops are with adjacent reentry but half of them are loose. The resulting density $\rho_a < \rho_c$ as in b, c, and e.

a rigid adherence to one extreme model.

In any theoretical model suggested for the folding one has to take care that it does not contradict any well-established experimental observation of the crystals. This is not a proof of the correctness but only a limitation imposed on any acceptable model.

Since the majority of the data were collected on LPE this article will be restricted to consideration of this special case.

Space Requirement of the Amorphous Layers at the Fold-Containing Surfaces of Lamellae

Some theoretical considerations about the space requirement of chains in the crystalline and in the amorphous state[1a,2] make the perfect fringed micelle model untenable (Figure 1a). If the straight stems in the crystal lattice are perpendicular to the lamellar surface, a little more than half the chains extending from the crystal interior to the surface of the lamella must fold back immediately in order to permit random arrangement of the chains in the amorphous layers separating subsequent lamellae. According to Flory, the fraction of stems ending in a loop with immediate reentry is $1 - \rho_a\langle|\cos\theta|\rangle/\rho_c$, where ρ_a and ρ_c are the densities of the amorphous and crystalline component, respectively, and θ is the angle between the chain segment and the amorphous phase continuation of the direction of the chains in the crystal lattice.[2] If the boundary between the crystalline and amorphous phase is not perpendicular to the crystal stem direction but at an angle 90° − φ the fraction of such loops is reduced by the factor $\cos\varphi$ to $1 - \rho_a\langle|\cos\theta|\rangle/\rho_c \cos\varphi$. No folding back is required if φ is larger than 65°. In such a case even the fringed micelle model with all the chains of the crystal lattice going from one lamella to the next one is not excluded.

With the interface perpendicular to the chain direction in the crystal lattice, $\varphi = 0$, one may reduce the fraction of immediate back-folding by increasing $\langle|\cos\theta|\rangle$. In the extreme case of a liquid crystal structure all chains in the amorphous layer may be almost parallel to the normal of the interface yielding $\langle|\cos\theta|\rangle \sim 1$ so that only $1 - \rho_a/\rho_c$ chains have to fold back immediately in order to allow the establishment of the amorphous phase. But experiments on swelling of the amorphous layer definitely exclude the liquid crystal model. A liquid crystal with chain axes of the macromolecules normal to the interface would expand laterally on swelling or would not swell at all if such an expansion is not possible. The experimental data show instead that swelling takes place[3] and that it increases the thickness of the layers[4] which is only possible if the chains in the surface layer are not fully extended, i.e., not arranged as in a liquid crystal.

The restriction is still more severe. Space needed for amorphous chains can be created only if many chains reentering a crystal fold back with adjacent reentry to form loops that are as regular and as short as possible. The remaining chains, however, may form loose loops with adjacent or random reentry, may form free/ends (cilia), or may form tie segments going to the next crystal. The above analysis is compatible with all these possibilities.

A more precise and simplified description of this analysis is shown in Figure 1b,c. At least half the stems in the crystal lattice must originate from regular adjacent reentry of a long chain molecule.[2] The regular loops with adjacent reentry alternate with two stems starting a larger loop corresponding to an adjacent or random reentry. In the figure one can connect free ends of the stems into loops of both types of reentry, tie molecules or cilia. If the rest of the chain is long enough it may form a loose loop or a tie chain. A short tail of a molecule only yields a cilium. On the opposite side of the lamella adjacent reentry loops may be either attached to the stems having random reentry on the first side (Figure 1b) or displaced to the left or right by one stem (Figure 1c). In the former case there are two and in the latter case at least three parallel stems belonging to the same molecule.

Nothing prevents formation of a larger number of adjacent reentries yielding a larger cluster of parallel stems belonging to the same molecule as long as the remaining loops are random. If all of them are regular no amorphous layer is possible.

In many respects such a model combines adjacent and random reentry in a manner which is practically identical with a combination of both reentry concepts that are derivable from small-angle scattering of slow neutrons discussed at the end of this article. Such an agreement certainly proves the deep insight into the fine structure of crystalline polymers at a time when such detail was ignored and chain folding was considered to consist of almost uniquely regular folds with adjacent reentry.

The existence of chains going from one crystal to the next, i.e., of tie molecules, is implied by mechanical cutting experiments on the crystalline polymer solid.[5] The cut goes mainly through the amorphous areas which offer a substantially smaller resistance than the crystals with densely packed parallel chains. The crystal can be cut only by rupturing all the chains in the path of the cut if the cut is perpendicular to the chain direction and by separating parallel chains and cutting only the loops at the surface if the cut is parallel to the chains. Hence in going through the amorphous layers and through the crystals parallel to the chains the knife cuts the tie molecules and the loops which are in the path of the cut. The ruptured chains are detectable by ESR which shows a small density of such chains per unit area of the cut. If all these chains were tie molecules one estimates that between 1 and 3% of the straight chain stems in the crystal lattice continue as tie molecules, i.e., go from one crystal to the next one.[6] This fraction has to be reduced by the number of chain loops ruptured if the cut goes partially through the crystals in the direction parallel to the chains.[6a,2]

Basic Effects Depending on the Fold Conformation

In this section the effects depending on the conformation of chain folds will be analyzed. The space requirement of rigid loops, crystallization kinetics, annealing, drawing, fractionation during crystallization, and the long period growth will be considered in their relationship with adjacent and random reentry.

The space requirement of rather rigid loops with adjacent reentry consisting of a minimum number of consecutive gauche conformations (Figure 1d) seems to impose the pyramidal habit on LPE single crystals growing from a dilute solution[7,8] at moderate supercooling. The majority of loops must be of this type in pyramidal crystallites. Formation of tight loops strains the crystal lattice because the ends of a loop with 5 or 6 consecutive gauche conformations do not fit exactly the ends of the corresponding straight stems of the crystal. The *ab* plane of the unit cell determined by wide-angle X-ray scattering[9] shows dilation effects which decrease by $1/L$. The dependence of the distortion on the inverse thickness of the lamellae indicates that the origin of distortion is in the surface of the lamellae, i.e., in the loops at this surface.

The model involving adjacent reentry and regular folds is a convenient basis for predicting the growth rate of the crystal lamellae which mainly depends on the rate of deposition of the first stem on a smooth growth face (secondary nucleation) and on the rate of filling the whole face with adjacent parallel stems (tertiary nucleation).[10] In the last process each stem has to be pulled out of the liquid and deposited individually on an existing ledge on the growth face of the lamella. Deposition proceeds extremely fast. It is only impeded by the need to supply end surface free energy and a need to pull the chain from the melt or solution.

Such a concept requires viscous resistance against chain transfer from the liquid to the growing crystal in order to explain the decrease of the rate of growth at very high supercooling. The activation energy for such a viscous transfer turns out to be less than that in conventional viscous flow. This is understandable because one does not shear the whole liquid, including entanglements, as happens in normal viscous flow, but one lets the chain move out of the liquid and entanglements in a reptatious motion.[11] This type of motion increases the viscous resistance with increasing molecular weight M by M^2 instead of by $M^{3.4}$ as measured in a conventional viscosity experiment with samples having a molecular weight greater than the entanglement molecular weight, $M_e = 8000$. Also, the activation energy in the case of crystallization, about 6000 J/mol, is only a fraction of the value obtained in conventional viscous flow because it is not necessary to move, destroy, and re-form the whole network of the highly entangled liquid but only to pull the chain out of the entanglements.

Random reentry requires less ordering and pulling of chains from a highly entangled random conformation in the melt or in a concentrated solution in order to build the crystal. The requirement is particularly reduced if one assumes that the randomly coiled macromolecule is simply solidified on the surface of the growing set of parallel crystals without any substantial chain displacement. The crystallization rate would be so fast that the chains cannot substantially change their entanglements with other chains and hence would crystallize where they were in the melt.[12] Thus the topology of copiously interspersed chains in the liquid state must be largely conserved during the process of crystallization, with preexisting entanglements concentrated in the noncrystalline regions. In this connection note the experiments on the crystallization of LPE from the glassy state.[13]

Annealing of single crystals forms an amorphous surface layer which is thicker than one can explain by loops with adjacent reentry.[14] It turns out that the length of the loops which determines the thickness of the amorphous layer increases very rapidly with the distance between the points where loops are fixed in the crystal lattice. A finite fraction of loops, between $^1/_3$ and $^1/_4$, must show random reentry in order to produce the observed thickness of this amorphous layer which seems to depend exclusively on the temperature of the annealing.[15]

Drawing of the crystalline polymer solid is extremely difficult to imagine if all reentries are random, because it is practically impossible to form well-observable microfibrils from a lamella with a perfect switchboard arrangement of loops. Even if one assumes that during the drawing process crystals of the original lamellar structure melt completely,[16] such a complete melting would not disentangle enough overlapping loops for incorporation of crystalline blocks into microfibrils. On the other hand one knows that the work of deforming forces, about 85 J/g for drawing at 60 °C at a rate of 0.5 cm/min, is not sufficient for raising the local temperature to the ideal melting point of the unstrained material and still less for supplying of the melt enthalpy of about 260 J/g.[17]

The role of entanglements is best demonstrated by drawing samples of increasing molecular weight. Samples of a weight average molecular weight up to about 200 000 show an extremely wide range of draw ratio, λ. At 60 °C they can be drawn to $\lambda = 30$[17] and at 70 °C and higher up to $\lambda = 50$.[18] Correspondingly, one obtains a high axial elastic modulus, E, up to 70 GPa, which seems to be an almost linear function of the draw ratio. Higher molecular weight samples draw to a much lower λ. At $M = 1.5 \times 10^6$ the λ is below 6 and consequently one cannot achieve a high E.[19] A reduction of the entanglement density can be achieved by casting films from a very dilute solution. If one chooses a 5% solution one increases the entanglement length by a factor of 20 and by a similar factor reduces the number of entanglements. Such a material can be drawn to $\lambda = 30$ in spite of the high $M = 1.5 \times 10^6$. It has a high elastic modulus and an axial elastic strength that is threefold higher than that of the medium molecular weight samples ($M = 10^5$).[20]

Although drawing experiments do not provide a limit to the fraction of random reentry loops, they are inconsistent with the perfect switchboard model of the surface loops on the crystal lamella. On the other hand, loops with adjacent reentry do not hamper drawing at all. Hence a structure with regular folds was used as the basic model for a description of drawing although it is not a condition for it.

The just-mentioned drawing experiments[20] also very clearly demonstrate the partial retention of the liquid-state entanglements during the crystallization. This is reflected in the dependence of the crystallinity on the weight-average molecular weight of the LPE. One obtains a high crystallinity, about 0.8, in samples with M about 10^5. Increasing M to 10^6 or higher yields a substantially lower crystallinity, about 0.5 or even less. Such a decrease is assumed to be the consequence of the fact that the entanglements cannot be included in the crystal lattice. The crystallization of such a high molecular weight sample from dilute solution, however, yields a material with a crystallinity close to that obtained with medium molecular weight samples.[20]

Fractionation during crystallization from the melt or solution is more sensitive to the conformational structure of the loops. Subsequent deposition of completely independent straight sections of a macromolecule would yield a fractionation at molecular weight M_1 of the single stem. All molecules smaller than M_1 would be rejected during crystallization. They would remain in solution or in the melt which has not yet crystallized. All larger molecules would be incorporated in the crystals.[21] The inclusion would not be perfect in the case of adjacent reentry since the excess over nM_1, with n a natural number, would remain as a cilium. In the case of random reentry such an effect will be important between M_1 and $2M_1$ but would not play any role at a larger M since the excess length can easily be incorporated in the random loops. Experiments,[22] however, show a fractionation extending up to between $3M_1$ and $4M_1$ which is completely incomprehensible in terms of a perfectly random reentry model. Also the adjacent reentry model cannot explain such an effect if one adds each stem individually to any existing ledge on the growth surface. In such a case one would reject all $M < M_1$ and, as a consequence of the looseness of the loops, would reject a gradually smaller fraction of molecules with their M between the aliquots of M_1. The average of all the rejected species up to $M = \infty$ ought to give the experimentally observed value between $3M_1$ and $4M_1$. Such a fit can be achieved but cannot be accepted as support for the model of adjacent reentry.

A similar situation occurs with the long period growth during annealing. Over a wide range one can write[23]

$$L(t) = A + B \log (t + t_0)$$

with a finite positive but very small t_0. The increase of the long period is a linear function of the logarithm of the time of annealing. The initial length $L(0) = A + B \log t_0$ corresponds to that of crystals before the annealing. The slope B strongly depends on the length of the macromolecule. The sections at the ends of the macromolecule have to be moved toward the center of the chain so that all the straight stems in the crystal become longer. This is a very slow process requiring more time with longer molecules. For strictly adjacent reentry one has $B \sim M^{-3}$ which means an extremely rapid decrease of the long period growth with increasing molecular weight of the sample.[24] No such effect was ever observed in an LPE with M's of 52000 and 520000.[25] In completely random reentry the molecular weight effect disappears completely because the supply of additional chain segments to each stem can be provided by loose loops which connect the stem with the rest of the macromolecule. Hence the total length of the molecule, i.e., its molecular weight, does not play any role in the long period growth as long as the loops are still sufficiently loose.

Small-Angle Neutron Scattering

The situation has changed quite appreciably with the advent of neutron small-angle scattering.[26] One can consider the conformation of an isolated deuterated macromolecule in a protonated matrix of otherwise identical molecules or vice versa. The information obtained can be applied to the average dimensions of the single molecule in the bulk if one assumes that deuteration has not changed the properties of the macromolecule and its interactions with the matrix. This requires that the deuterated and protonated macromolecules behave in exactly the same manner. This is not completely correct as can be seen from the relatively large shift of the melting or crystallization temperature if one goes from protonated to deuterated LPE.[27] Such a shift raises some suspicion about the validity of conclusions derived from neutron scattering on such mixtures. The small difference in the chemical potential of H and D may lead to some fractionation or phase separation which distorts the interpretation of the scattering data. The average dimensions and conformations of deuterated macromolecules determined by neutron scattering may differ from those of a protonated macromolecule in the same matrix because one has measured the scattering of a whole complex of aggregated molecules rather than that of a single molecule. In addition the conformation of the deuterated macromolecule is affected by the surrounding protonated macromolecules in a different way than a protonated macromolecule would be affected. Moreover, this difference varies if one goes from the melt or solution to the solid state because the average distances between the chains change as a consequence of such a transition.

The large difference in the measured long period L of the 100:0 (L = 22 nm), 50:50 (L = 20 nm), and 0:100 (L = 17 nm) mixtures of the protonated and deuterated PE[27a] makes one suspect that the materials used were partially branched. Since branching affects the crystallization and hence the SANS, interpretation of the scattering curves is more complicated.

If one neglects the above possible deviations one can summarize the results obtained on relatively low concentrations of deuterated or protonated macromolecules of LPE as follows.[28] The gyration radius and the angular dependence of the scattering intensity in the melt or concentrated solution do not differ markedly from those in the crystalline state which was obtained by rapid quenching from the melt. In the solid state the scattering can be described as originating from single stems in the crystal lattice connected by random loops of a length one would expect if the loops had a rather random conformational distribution but were partially reflected on a layer relatively close to the crystal core of the lamella.[29] Such a model nearly doubles the density of the amorphous layer on the boundary between the amorphous layer and the crystal core of the lamella.[30] This is a natural consequence of neglect of the original analysis by Flory[2] of the space requirement of amorphous chains which requires that a little more than half the stems of the crystal belong to regular loops with adjacent reentry.

But one can also describe the observed gyration radius and the angular dependence of the scattering intensity by assuming a system of clusters containing about three adjacent stems separated by random loops[30] (Figure 1e). This means that about a third of the stems are connected by loose loops with random reentry. However, a model with exclusively adjacent reentry and regular or loose loops[10] (Figure 1f) does not yield the experimentally measured gyration radius and the angular dependence of the scattered intensity.[28] Note, however, that the neutron-scattering data were obtained on a quenched sample. Hence all the conclusions and particularly the crystallization model apply only to samples solidified from the melt at very high supercooling. It is too early to apply the cluster model indiscriminately to slowly cooled samples and to samples crystallized from dilute solution at small supercooling.

Fold Model with Partial Adjacent Reentry

The model with adjacent chain clusters separated by random reentry loops seems to explain rather easily not only the geometrical requirements of chain conformation in the crystalline state as derived from the small-angle neutron scattering but also other experiments mentioned above.

There is not too much to change in the kinetics of crystallization and the dependence of crystal growth rate on supercooling.[31] Since the neutron-scattering data only apply to quenched samples one has to consider effects relating to high supercooling, i.e., the regime II of crystallization, where nucleation events are rapid relative to strip completion rates, which demands the deposition of independent clusters of stems.

Reduction of the number of random loops increases the possibility of plastic deformation during the drawing. The formation of microfibrils, already mentioned, does not require adjacent reentry exclusively although it becomes practically impossible with a completely random reentry which results in so great an entanglement density that a microfibril cannot be formed from blocks torn out of the fractured lamella.

The most important support of the compromise model comes from fractionation, from the thickness of the amorphous layer on the surface of the lamella containing the chain folds which become established during the annealing of single crystal mats, and from the dependence of the long period growth on molecular weight.

During crystallization, clusters of about three adjacent stems are attached to the growing face and are again dissolved by the adjacent melt or solution. The crystal grows if the former effect prevails over the latter one and dissolves in the opposite case. If such a cluster is larger than the whole molecule it has a higher probability of being detached and a smaller probability of being formed than in the case where the molecule is larger than such a cluster. A longer molecule has a much better chance of becoming reattached if it also has the additional probability of remaining attached to the growing crystal by a cluster on the rest of the chain. This makes crystallization easier for chains that are larger than three stem clusters and still easier for longer molecules which can form more than one cluster. Hence one finds in the remaining solution or melt a larger fraction of molecules shorter than three to six M_1 and finds in growing crystals a smaller fraction of such molecules. The opposite is true for longer molecules. This agrees exactly with the experimental data in contrast to models of a perfect adjacent or completely random reentry.

As already mentioned, the amorphous surface layer on lamellae obtained by annealing of single-crystal mats is thicker than one can explain by the random length of loose loops with adjacent reentry. This is in very good agreement with the cluster model[30,31] which assumes that about one-third of the stems are connected by loops of random reentry.

In long period growth during annealing at a temperature which is still below the melting point of the crystals, the increase in the thickness primarily depends on the rate of supply of chain elements from the ends of a macromolecule toward its center. In a crystal with small clusters one can supply segments from random loops to clusters between the loops. Since segments have to be transported over only half the length of such a cluster, the total molecular weight has no effect as long as the supply can be provided by the loose loops between two consecutive clusters of the same molecule. This seems to suffice during the usually reported experimentation times because the crystal thickness does not increase by a very large factor. Moreover, this process comes to an end as soon as the supply of segments from random loops is exhausted. The further supply of segments over a longer distance in the crystal lattice soon becomes so slow that the corresponding long period growth becomes undetectable. Very likely this happens with all samples which after a while reach an almost constant thickness.[25]

Conclusions

One sees that the compromise model of chain folding with partial adjacent and partial random reentry explains in a straightforward manner practically all observations on polymer crystals. It is indeed reassuring that both contrasting concepts can and must be combined in order to understand the basic effects of neutron scattering, the fractionation by crystallization, the formation of the relatively thick surface layers, and the long period growth during annealing. Moreover, this model is consistent with the original suggestion by Frank and the analysis by Flory of the space requirement of chains in amorphous layers between parallel crystal lattices which makes the fringed micelle model untenable and requires that about half the straight stems of the crystal core be connected by perfectly ideal regular folds with adjacent reentry.

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Articles

Synthesis, Charge Transfer Complex Behavior, and Electronic Transport Properties of Novel Electron-Acceptor Polymers Based on Trinitrofluorenone

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ABSTRACT: Two novel aromatic electron-acceptor monomers based on the trinitrofluorenone nucleus have been synthesized and polymerized. These monomers, glycidyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (I) and 2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate (II), were synthesized by coupling 4,5,7-trinitro-fluorenone-2-carboxoyl chloride with glycidol and 2-hydroxyethyl methacrylate, respectively. Polymerization was initiated by acidic ring-opening catalysts for I and by standard free-radical techniques for II. The electronic transport characteristics of the resulting low molecular weight polymers were investigated by a photodischarge technique. The charge transfer complex behavior of poly(2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate) was studied by utilizing *N*-isopropylcarbazole as donor.

Electron-acceptor polymers are of interest from a fundamental standpoint because of their potential to serve as electron transport molecules vis-à-vis the hole transport exhibited by electron-donor polymers like poly(*N*-vinylcarbazole). Specifically, the electron acceptor 2,4,7-trinitro-9-fluorenone (TNF) is known to possess excellent electron transport properties under an applied electric field in an amorphous film or in a polymeric matrix.[1] Therefore, polymers containing TNF would be of interest for their electron transport characteristics.

However, while the literature abounds with examples of electron-donor polymers, very few examples of electron-acceptor polymers have been reported. Most examples of electron-acceptor polymers have been prepared by step-growth techniques as exhibited in the reports of Schulz and Tanaka[2] and Sulzberg and Cotter.[3] Poly(2,4,7-trinitro-9-fluorenyl methacrylate), which we recently reported, is an example of an electron-acceptor polymer prepared by chain-growth techniques.[4]

The reasons for the lack of examples of electron-acceptor polymers are obvious. Conventional addition polymerization reactions become problematic in the presence of a strong electron acceptor. For example, for TNF-containing monomers, anionic polymerizations would fail because of electron-transfer reactions. Free-radical polymerization of most polymerizable groups would likewise not be promising because of electron transfer or other free-radical-inhibition processes by the nitro aromatic. Cationic techniques would appear feasible, but the monomer synthesis would require the incorporation of an electron-rich polymerizable group into a structure containing an electron poor acceptor—a potentially unstable situation.

This paper discusses the synthesis and polymerization of two TNF-containing monomers designed to circumvent the polymerization problems discussed above. The first monomer, glycidyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (I), was designed to use ring-opening polymerization. The second monomer, 2′-ethylmethacryl 4,5,7-trinitro-9-fluorenone-2-carboxylate (II) was chosen because the chain transfer of methacrylate to aromatic nitro compounds has been reported to be relatively small.[5] Our successful polymerization of 2,4,7-trinitro-9-fluorenyl methacrylate bears this point out.[4]

The electronic transport characteristics of these polymers and a model compound *n*-butyl 4,5,7-trinitro-9-fluorenone-2-carboxylate (III) were measured and compared to those reported for TNF. The charge transfer complex characteristics of these strong electron-acceptor polymers were also investigated.

Experimental Section

Monomer Synthesis. 4,5,7-Trinitrofluorenone-2-carboxylic Acid. This compound was synthesized by the method of Sulzberg and Cotter.[6]

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