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Thermal Analysis of the Conformational Disorder in Semicrystalline Poly(vinylidene fluoride) and Poly(trifluoroethylene)

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ABSTRACT: Differential scanning calorimetry was used to explore the changes in heat capacity and latent heat of poly(vinylidene fluoride) and poly(trifluoroethylene) between the glass and melting transition temperatures. In contrast to more rigid polymers, poly(fluoroethylenes) show no detectable "rigid amorphous" fraction. Evidence of conformational disorder (condis crystals) in both polymers is discussed. For poly(vinylidene fluoride) a condis glass transition is proposed to exist at 360 K for the α-crystal form. A condis to condis crystal transition on cooling seems to occur at 350–360 K. A third level of conformational order that is involved in the ferroelectric properties of poly(vinylidene fluoride) can be forced by an electric field above about 380 K (poling), but it remains frozen (glassy) up to the melting temperature, i.e., there is no Curie temperature. Semicrystalline poly(trifluoroethylene) is also known to have a conformationally disordered structure. Above the rather broad glass transition it already has the heat capacity expected for the liquid, an indication that amorphous and condis glass transitions may overlap in the temperature range from 230 to almost 400 K.

Introduction

In a major thermal analysis effort of linear macromolecules the ATHAS data bank of heat capacities was established.[1] This data bank has served as a basis for the interpretation of thermodynamic properties. In this connection the heat capacities of all poly(fluoroethylenes) in the solid state were linked to their frequency spectra[2] and the heat capacities of the liquid states were measured and united in an empirical addition scheme, capable of predicting C_p starting from the glass transition temperature to decomposition.[3]

With the heat capacities of the limiting amorphous and crystalline states known to a precision of better than ±5%, it is now possible to discuss the properties of the semicrystalline polymers. In this paper we will present measurements on partially crystallized poly(vinylidene fluoride) (PVF2) and poly(trifluoroethylene) (P3FE). The results are linked to the possible existence of conformational disorder (condis crystallinity)[4] in these polymers. Since at low temperature the polymers show frozen disorder, there should be glass transitions of the condis states.[4]

To get some insight into the possible conformational disorder, the molecular mechanics of a single PVF2 chain was calculated before, estimating electrostatic, torsional, and van der Waals interactions of a 32 carbon atom chain section.[5] The results of this computation were that the isolated PVF2 chain does not have, as one might expect, two distinct potential energy minima close to the basic $TGT\bar{G}$ conformation of the α-crystal form. For poly(tetrafluoroethylene) (PTFE),[6] in contrast, two distinct trans-conformation minima exist at a ±15° rotation angle and provide the explanation for its condis crystallinity between 303 and 605 K.[7] The isolated PVF2 chain may instead assume a bond angle between 114° and 118° and torsional angles of the gauche conformations between 40° and 80° *without* major changes in potential energy (<1 kJ/mol).[5] Intermolecular constraints of the crystal must thus fix the observed conformations at lower temperature and conformational disorder similar to that in PTFE may well be expected at higher temperature. It will be shown below that condis crystallinity is likely to exist also in P3FE but that distinct differences exist between the poly(fluoroethylenes) that are in need of detailed study by more motion-specific analysis techniques such as dielectric or NMR methods.

Experimental Section

The poly(vinylidene fluoride) (PVF2) was obtained from Polysciences, Inc. Its molecular weight was 120 000 and by ^{1}H and ^{19}F NMR, 11% reverse addition was found. The as-received sample was a semicrystalline mixture of the α- and β-crystal modifications that converted to pure α on recrystallization (checked by X-ray diffraction).

The poly(trifluoroethylene) was an uncharacterized sample of sufficiently high molecular weight to have little influence on thermal properties.

All calorimetry was performed with a computer-interfaced Perkin-Elmer DSC 2. The analog output was converted to digital form with a Nelson Analytical, Inc., Model 860 voltage-to-frequency converter. Details of the computer software (IBM XT personal computer) were developed by Laboratory Microsystems, Inc. More detailed description of instrumentation and computation have been published earlier.[3] Sampling length of data was 0.5 s, 15–25-mg samples were enclosed in aluminum pans. Sapphire reference material was used. The temperature range of measurement was from 220 to 500 K. The calorimeter was thermostated at about 200 K with a mechanical refrigeration unit. All runs were made at a heating rate of 10 K/min in a dry nitrogen environment.

We also used the Perkin-Elmer DSC 2 for crystallization experiments with cooling rates between 5 and 80 K/min.

Du Pont thermal analyzers (types 990 and 900) were used for evaluation of glass transition temperatures and for crystallization runs on very fast cooling.

Results

Typical DSC curves of PVF2 and P3TFE are shown in Figures 1 and 2. Included in these figures are the calculated heat capacities of the solid, liquid, and semicrystalline samples. The data for the solid are computed from the approximate vibrational spectrum as outlined in detail in

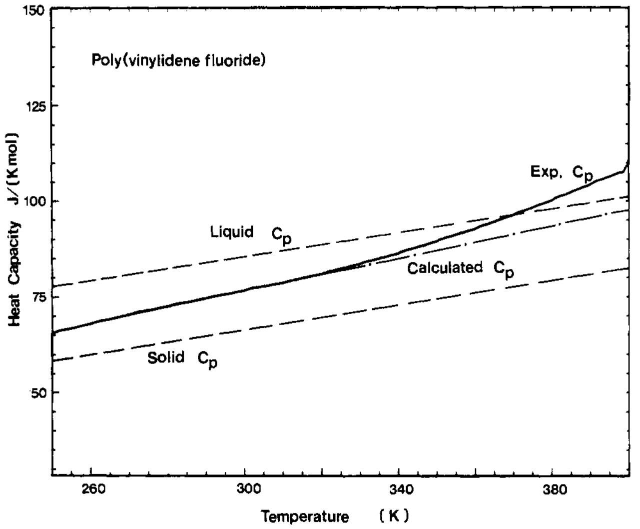

Figure 1. Heat capacity of semicrystalline PVF2 from 250 to 400 K. The data for the liquid state are computed from the equation given in ref 3. The data for the solid are computed from the approximate frequency spectrum as given in ref 2. Melting begins to the right of the given temperature interval, the glass transition is to the left ($T_m° = 483.2$ K, $T_g = 233$ K).

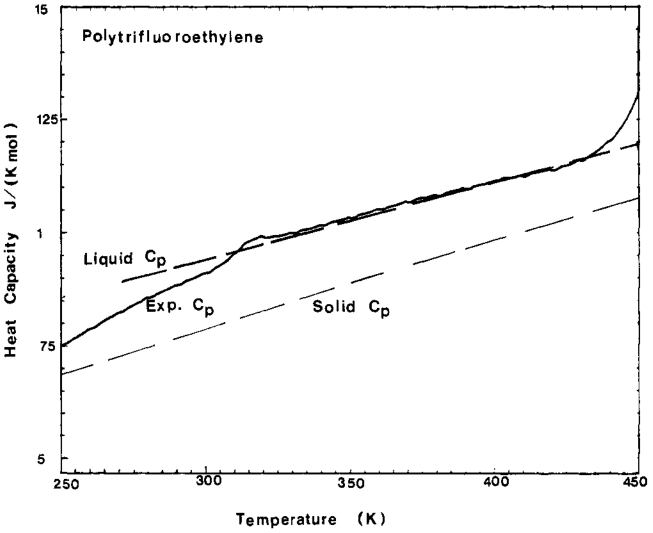

Figure 2. Heat capacity of semicrystalline P3FE from 250 to 450 K. The data for the liquid state are computed from the equation given in ref 3. The data for the solid are computed from the approximate frequency spectrum as given in ref 2. Melting begins to the right of the given temperature interval, the glass transition is shown on the left ($T_m° = 495.2$ K, $T_g = 304$ K).

ref 2. The data for the liquid were estimated from the addition scheme derived for all liquid poly(fluoroethylenes):

$$C_p(\text{liquid}) = N_F(104.8 + 0.0568T) + (1 - N_F)(36.9 + 0.0854T) \quad (1)$$

in J/(K mol) for temperatures above 480 K and

$$C_p(\text{liquid}) = N_F(55.0 + 0.162T) + (1 - N_F)(37.7 + 0.0829T) \quad (2)$$

in J/(K mol) for temperatures below 480 K to the glass transition.[3] The fraction of fluorination, N_F, is 0.5 for PVF2 and 0.75 for P3VF. Measured heat capacities in the temperature interval between the upper end of the glass transition and the begining of condis crystal mobility could be fitted into a linear dependence with crystallinity w^c:

$$C_p(\text{semicrystalline}) = w^c C_p(\text{solid}) + (1 - w^c)C_p(\text{liquid}) \quad (3)$$

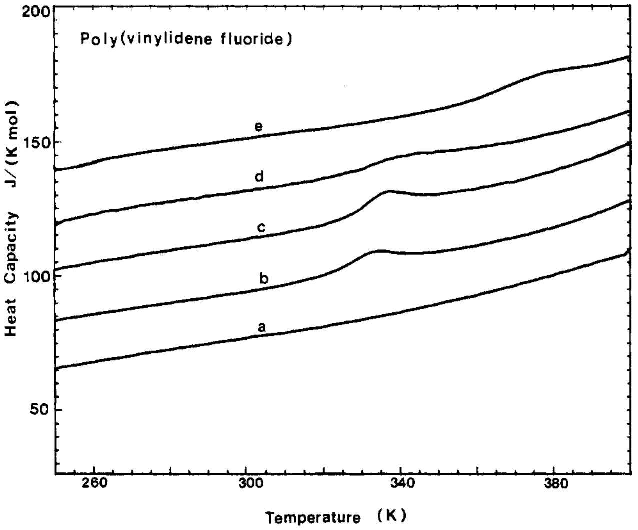

Figure 3. DSC runs of PVF2 with different thermal histories. Consecutive curves are shifted by 20% (18 J/(K mol)): (a) cooled at 10 K/min; (b) cooled quickly from the melt to room temperature; (c) quenched in liquid nitrogen from the melt; (d) isothermally crystallized at 440 K then quenched to room temperature; (e) annealed for 2 days by cooling slowly from 335 to 315 K after initial cooling from the melt at 10 K/min, final cooling to room temperature at 0.5 K/h.

Crystallinities were established through comparison of measured heats of fusion with known data for complete crystallization (6.70 kJ/mol at 483.2 K for PVF2 and 5.44 kJ/mol at 495.2 K for P3FE). For PVF2, nine data sets with crystallinities from 42% to 64% fit eq 3 within ±5% in the temperature range 260–310 K. For P3FE, six samples with crystallinities between 11% and 16% fit eq 3 within ±2% in the temperature range 330–410 K.

PVF2 was analyzed also as a function of heat treatment. Figure 3 summarizes these data. A small endotherm between 320 and 350 K is observed for certain thermal histories. In general, no such endotherm is observed in samples cooled at ≤10 K/min or crystallized isothermally at temperatures between 330 and 390 K (curve a). Crystallization above 400 K followed by quick cooling or direct quenching from the melt always leads to such small endotherms (approximately 150–200 J/mol, curves b–d). Extremely slow cooling does not shift the peak, as would be expected for an annealing peak,[8] but introduces a C_p jump at about 360 K [7 J/(K mol), 50% crystallinity, curve e].

Figure 4 shows the effect of annealing at 350 K on the structures causing the small endotherm between 320 and 350 K. Annealing times varying between 0 and 3 h did not affect the second heating curve. Annealing at room temperature, which is only little below the beginning of the endotherm, for several days did not result in changes in the endotherms shown in curves a, b, and d of Figure 3.

Figure 5 illustrates the thermal behavior on cooling from the melt. Besides the main crystallization exotherm there is a shallower, second exotherm at about 350–360 K. At very fast cooling rates of about 2000 K/min, as may be reached in liquid nitrogen quenching, we could observe that the major crystallization occurred below 300 K. These fast cooling experiments were carried out with a special high-speed DSC, described in detail in ref 9.

Data on the glass transition temperature of PVF2 were deduced from 24 runs of different crystallinity by using a Du Pont 990 thermal analyzer. The beginning of the glass transition is detectable at 175 K, the end, at 241 K, and the midpoint, at 233 K. For P3FE the complete glass transition range was within the heat capacity measurement

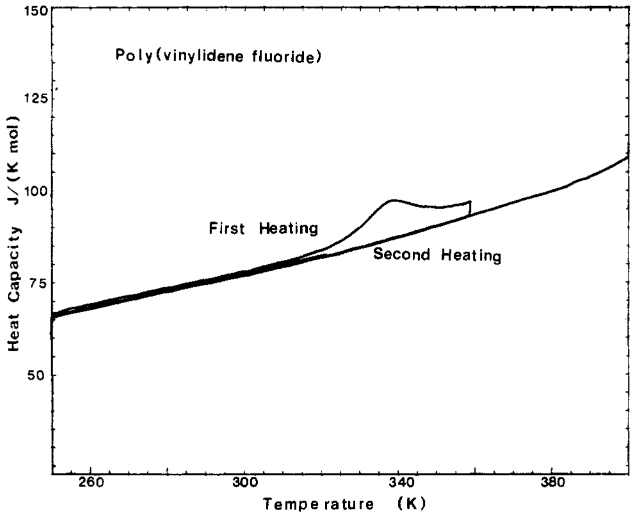

Figure 4. Effect of higher temperature annealing on the transition at 330 K. The original sample was quenched to room temperature and then heated to 360 K at 10 K/min (curve labeled first heating), then cooled at 320 K/min, and reheated at 10 K/min (curve labeled second heating). The second heating shows no endotherm.

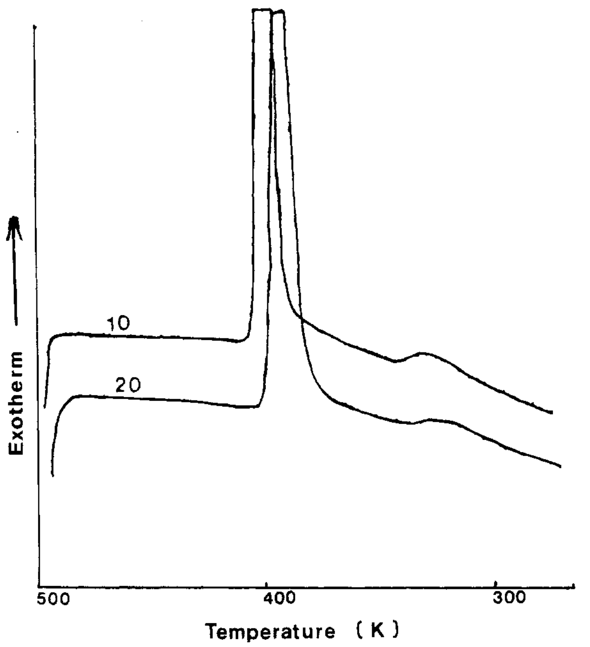

Figure 5. Crystallization of PVF 2 on cooling at 10 and 20 K/min (recorded with a Du Pont DSC).

range (Perkin-Elmer DSC 2). The beginning can be seen at 230 K, the end may be as high as 400 K (see Figure 2) and the point of half-devitrification, taken as T_g, is at 265 K.

Discussions

The additivity of heat capacity according to eq 3, from 240 to 310 K for PVF2 and approximately from perhaps 320 to 410 K for P3FE, is an indication that there is, within experimental precision, no "rigid amorphous" portion above the glass transition temperature. The influence of the crystalline areas on the amorphous contributes, at most, to the broadness of the glass transition. Similar broad glass transitions are also observed for polyethylene[10] and poly(tetrafluoroethylene).[11] In other words, between the transition regions for the glass and crystal, the amorphous fraction has reached full mobility and the heat capacity of the crystalline fraction is fully described by the vibrational motion in the solid state.[2] Polymers which show a rigid amorphous fraction are often the stiffer chain polymers such as poly(oxymethylene),[12] poly(ether ether ketone) (PEEK)[13], poly(oxydimethylphenylene) (PPO),[14] and poly(thiophenylene).[15]

Of interest, in particular for PVF2, is the possible conformational mobility in the crystalline state. There is only one other thermal analysis of PVF2 in the literature.[16] The writers observed also the small endotherm at about 340 K, but did not study it further. They reported, in agreement with the present experiments, that the endotherm appears only in quenched materials. The interpretation of the endotherm was different. They proposed an "upper glass transition" of the amorphous portion of the system. This follows Boyer's idea[17] of the existence of "upper" and "lower glass transitions". Some experimental facts do not, however, agree with such an interpretation. First, the heat capacity has reached already at 240 K the value that is expected from eq 3; i.e., there is no possibility of further increase in C_p. Second, there is no clear reproducible heat capacity jump in the conventional way. The heat capacity at the transition temperature starts to deviate from the one calculated (see Figure 3). This can be the beginning of a transition. An upper glass transition, however, is associated with the end of a broad glass transition range. Third, the shape of the endotherm is not that of a glass transition with a hysteresis, rather that of a transition with a latent heat (a hysteresis peak should disappear for faster cooling than heating rates, which is not seen in Figure 3). Last, the glass transition should remain observable on cycling through the transition region (see Figure 4), which is also not in agreement with observation.

A common interpretation of such small endotherms is that they represent an annealing peak.[8] Annealing peaks are usually found 5–20 K above the crystallization temperature or the temperature of holding of a prior poorly crystallized sample. Annealing peaks are known for PVF2,[18] but at much higher temperatures (at about 430 K compared to the 320–350 K found here). Annealing procedures at lower temperatures are not able to introduce annealing peaks. Annealing at room temperature for example after cooling from the melt does not introduce an annealing peak. Further observations that make an interpretation of the 320–350 K endotherm as an annealing peak unlikely are the following: (1) Heating and cooling through the endotherm does not show the typical reversibility of an annealing peak (Figure 4); instead, once heated through the endotherm, it cannot be recovered; even long-term annealing at room temperature does not reintroduce the endotherm. (2) The endotherm does not shift in temperature with different crystallization conditions or on annealing. (3) The second, small crystallization peak in Figure 5 at 350–360 K is too high to be related directly to the endotherm in question. (4) Isothermal crystallization at temperatures between 330 and 390 K does not yield similar annealing peaks.

We would like to link this endotherm at 320–350 K to the conformational disorder in the PVF2 crystals. The α-crystal form present in the analyzed samples has been studied widely by X-ray and electron microscopic techniques.[19-23] The crystal structure is orthorhombic and probably of space group $P2_1/c$.[22] The chain conformation is well established as TGT$\bar{\text{G}}$, but the packing of such chains varies with the crystallization conditions.[23] Figure 6 shows the four possible orientations of the PVF2 chain in the crystal. Looking at the fluorine atoms, their orientation can be up ($\bar{\text{C}}$) or down (C) and predominantly left (A) or right ($\bar{\text{A}}$). A and $\bar{\text{A}}$ are interchangeable by rotation about the crystallographic c-axis; C and $\bar{\text{C}}$ are inter-

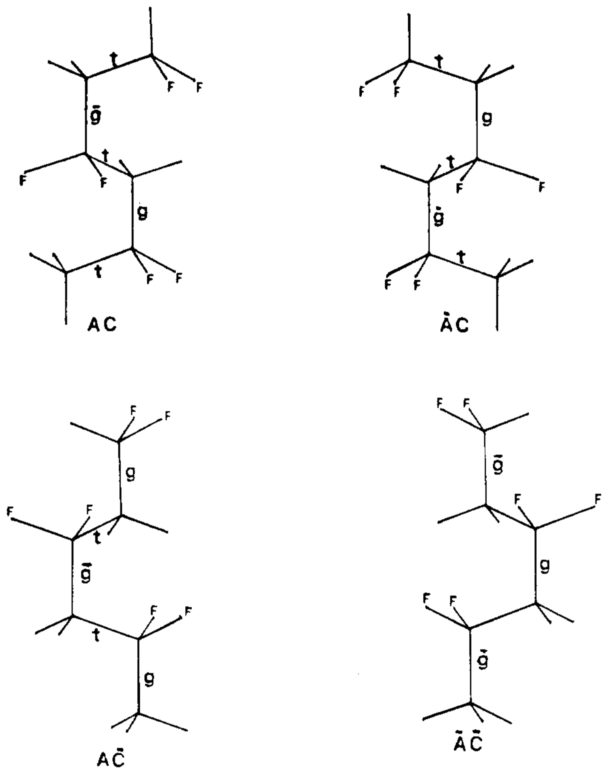

Figure 6. Four orientations of the chain of α PVF2.

changeable by reversal of the c-axis. Changes in these orientations for the whole chain of a crystal in a single step are impossible because of a too high activation energy and the connectivity of the chains at the crystal interface to chain folds and tie molecules. It is possible, however, to change the orientations through local conformational rearrangement, leaving at any time the major portion of the chain unchanged. If one now assumes the existence of a condis crystal, the conformations would be dynamically interchangeable. In case full crystalline order is not reached on cooling of the condis crystal, a (condis) glass transition should be observed.[4] Next, we speculate on such a two- or three-level condis crystallinity for PVF2 and a single-level condis crystallinity for P3FE.

The first level of condis crystallinity concerns the "up" and "down" equilibrium (see Figure 6). An interchange between $\mathrm{TGT\bar{G}}$ and $\mathrm{GT\bar{G}T}$ conformations that accomplishes such equilibrium was suggested by Miyamoto et al.[24] to be the cause of the dielectric α_c-transition at 363 K. This is in agreement with the X-ray data by Takahashi et al.[23,25–27] that indicate that the crystallographic c-direction shows gradual changes, beginning at 270 K, and a temperature-dependent up and down equilibrium above 370 K. On cooling, one expects thus that below 370 K the equilibrium freezes at a level determined by the cooling rate.

A second level of conformational disorder is thought to be the change in orientation about the chain. For this motion a rearrangement from $\mathrm{TGT\bar{G}}$ to $\mathrm{\bar{G}TGT}$ is needed according to Figure 6.[23] This motion seems to become possible at about 440 K. Such motion is also involved in the thermal transition from the α- to γ-crystal polymorph.[28–30]

A further, possibly third level of conformational disorder was proposed by Lovinger.[31] It involves the change TGTG to $\mathrm{T\bar{G}TG}$ and occurs upon application of an electric field above 380 K to obtain an oriented, polar form of the crystal. This change does not occur by thermal treatment; i.e., once poled, a sample remains ferroelectric. There is no Curie temperature below the melting temperature. The third level of conformational disorder is thus only available as a CD glass.

This conformational disorder in PVF2 and its mobility is now to be connected with the here presented thermal analyses. Nothing can be said about the third level in condis crystallinity. Its changes need the external forces of the electric field. It is present below the melting temperature only as a "glass". Its glass transition temperature must exceed T_m and is thus not measurable by thermal analysis.

The second level of condis crystallinity, associated with the change in orientation about the chain, unfreezes at about 440 K. This is also too close to the melting peak to make a clear thermal analysis.

This leaves the first level of condis crystallinity, supposed to unfreeze according to dielectric and X-ray data within the crystal between about 360 to 370 K. Close to this temperature (350–360 K) one observes a small exotherm on slow cooling after major crystallization (see Figure 5) and also a small endotherm between 320 and 350 K on heating after quick cooling and low-temperature crystallization (see Figure 3). Furthermore, the increase in C_p at about 360 K (Figure 3e) may be a direct indication of a glass-transition-like unfreezing within the crystal. In somewhat more detail, the crystallization exotherm could not be the polymers' common secondary crystallization of small crystals because of the missing corresponding melting peak that would have been expected at a 5–20 K higher temperature. One expects thus that the exotherm signifies an irreversible crystal reorganization that also freezes the up–down equilibrium. On fast cooling, crystallization occurs below the temperature of this crystal reorientation and one might speculate that the up–down equilibrium reaches a lower temperature value in the more disordered crystals or on their surfaces. On heating, this higher concentration of low-temperature conformations relaxes close to the glass transition temperature with an endotherm. Once relaxed, such an excess low-temperature conformations cannot be reintroduced in the once grown crystals. The equilibrium freezes with little hysteresis at the glass transition temperature as seen in Figure 3e at 360 K.

P3FE crystals were also found to have a conformationally disordered structure.[32] Mechanical and dielectric relaxation measurements indicated two transitions, one, designated α, at 323 K, and one, designated β, at 253 K. It was proposed that α is connected to the glass transition and β to local relaxation in both the crystalline and the amorphous phase. Figure 2 shows that the broad range of glass transition seen by thermal analysis covers both transitions, similar to the observations in polyethylene[10] and poly(tetrafluoroethylene).[11] The surprising observation in Figure 2 is that despite 20% crystallinity P3FE reaches already at about 400 K the heat capacity of the melt. Condis phases are known now to have often a heat capacity close to that of the melt.[4,33] It is thus possible that the glass transition range contains portions arising both from the melt and from the crystal. The conformational disorder in the crystal was shown by Lovinger and Cais[34] to be an irregular succession of TG, $\mathrm{T\bar{G}}$, and TT sequences.

Looking at all poly(fluoroethylenes) one can thus see a broad condis crystal behavior. Polyethylene has at high temperature and pressure a hexagonal condis phase with a large first-order disordering phase transition. In the condis phase a trans–gauche equilibrium close to that of the melt exists.[4] For PTFE the disordering transition occurs at room temperature and is smaller than in polyethylene. The equilibrium covers only the T(+) to T(−) equilibrium.[7] For PVF2 and P3FE successions of conformational disordering with relatively small energy differences are possible. Nothing seems to be known about possible conformational disorder in PVF.

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Registry No. PVF2, 24937-79-9; P3FE, 24980-67-4.

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Thermoplastic Elastomers by Hydrogen Bonding. 3. Interrelations between Molecular Parameters and Rheological Properties

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ABSTRACT: The properties of polybutadienes of narrow molecular weight distribution are modified by hydrogen bond interaction between 4-phenyl-1,2,4-triazolidine-3,5-dione (urazole) groups attached to the polymer backbone. The rheological properties of the modified polybutadienes are investigated as a function of the molecular weight and the degree of modification. The relaxation time spectra, obtained from the measured complex modulus G^*, are used to discuss changes in the rheological behavior. A broadening of the rubbery plateau zone and an increase of zero-shear viscosity and steady-state recoverable compliance J_e^0 are observed with increasing content of polar units. The hydrogen bonds between urazole units form a thermoreversible network. Due to the labile hydrogen bond linkages no rubber elastic equilibrium network modulus is observed in these systems.

Introduction

Thermoplastic elastomers are materials having properties similar to cross-linked rubbers at room temperature. At higher temperatures these materials are processable by common techniques convenient for thermoplastic materials. Generally two types of synthetic thermoplastic elastomers (TPE's) have been recognized. The first type includes SBS triblock copolymers and segmented block copolymers of the polyether–ester and polyether–urethane type. In these systems phase separation into a soft matrix and a rigid dispersed phase is responsible for the network structure. The hard-phase domains act as mechanical filler and multifunctional cross-links. The second type of thermoplastic elastomers is based on one-phase structures. The thermoreversible junctions are introduced by relatively weak interactions, which break at higher temperatures. The sulfonated EPDM's may serve as an example for this latter type.[1,2] In these systems thermoreversible cross-linking is achieved by the formation of aggregates of ionic dipoles. Until now the influence of the aggregate size on the final properties has not been studied in detail. Theoretical attempts to describe the viscosity and the dynamic behavior of ionomers assume the formation of dimeric aggregates.[3,4] Recent investigations on ionomeric model systems show that the number of associated dipoles may be larger than previously believed.[5] Another type of secondary valence interaction, capable of forming thermoreversible networks, is hydrogen bonds. This type of interaction is present in many biopolymer gels.[6] In contrast to the nondirected electrostatic interaction between ion dipoles, hydrogen bonds are oriented. In most cases only two distinct partners are involved in a hydrogen bond.

In order to investigate the complex phenomena associated with the formation and the properties of thermo-

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