$\mathcal{P}'(\bar{\varphi}_h,\Delta)$ the resulting matrix; (iii) $\mathbf{P}'$ is given by $\Delta/\pi \cdot \mathcal{P}'(\bar{\varphi}_h,\Delta)$. Since $S(n\pi)$ $(n \neq 0)$ is zero, if $\Delta = \pi$, $\mathbf{P}'$ reduces to the identity matrix, as it must be.

Concluding Remarks

The asr method may be easily adapted to the pseudo-stereochemical-equilibrium treatment of infinite copolymer chains. Results of the unperturbed dimensions obtained for atactic polypropylene show a substantial agreement with experimental data. They also show that the chain ensemble to which our calculations refer is very closely described by a Markoffian sequence of d and l units. As seen in previous calculations, a satisfactory convergence is obtained in the calculations if the Fourier expansion of the statistical weights is pushed up to terms of order about 10.

The authors would be glad to provide the whole set of the Fortran computing programs to anybody interested. They presently can perform the calculations reported in the present paper for any polymer, or copolymer, having $-\!(\text{A–B})\!-$ monomer units, provided its conformational energy may be given as a sum of terms each depending on two consecutive skeletal rotations.

Acknowledgment. The authors gratefully acknowledge useful discussions with Professor G. Moraglio of the Polytechnic of Milan. This work has been supported by the Consiglio Nazionale delle Richerche (CNR), research contribution No. CT.74.00726.03.

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Dielectric and Dynamic Mechanical Relaxations in 3,3,3-Trifluoro-2-trifluoromethylpropene (Hexafluoroisobutylene)/1,1-Difluoroethylene Alternating Copolymers

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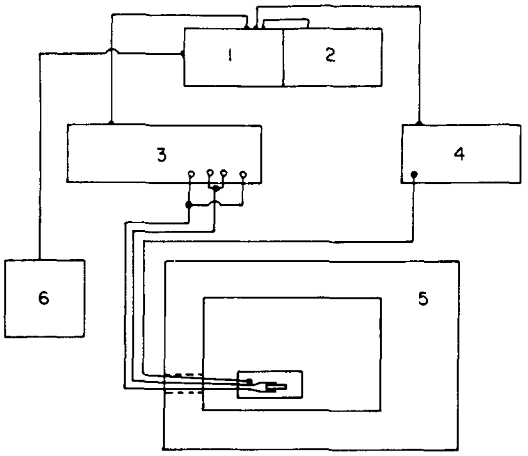
ABSTRACT: The α and β dielectric relaxations for an alternating copolymer of poly(vinylidene fluoride/3,3,3-trifluoro-2-trifluoromethylpropene) have been studied. It is proposed that these relaxations are the glass transition and a local mode motion of the polymer chain, respectively. The relatively high value of T_g (~405 K at 120 Hz) is discussed in terms of chain stiffness due to steric interactions and electronic repulsion. On the basis of the T_g relaxation in the copolymer, it is postulated that poly(3,3,3-trifluoromethylpropene) would probably possess an exceptionally high T_g. The β relaxation (205 K at 120 Hz) is assigned to a low amplitude motion of the main chain.

Fluoro- and perfluoropolymers have important industrial applications in that they exhibit high dielectric breakdown strength, are excellent insulators, and exhibit very low surface tension characteristics.[1,2] These materials exhibit the characteristic properties of many polymer systems in that they can be semicrystalline or amorphous and many of their dynamic properties (T_g and sub-T_g relaxations) can be related to their proton substituted counterparts.[3] Additionally, some of the crystalline polymorphs of these fluoropolymers exhibit piezo- and pyroelectric properties.[4,5]

Polytetrafluoroethylene (PTFE) has been widely adopted for industrial use. Unfortunately, thermal processing of PTFE is made difficult by its high viscosity (10^{11} P at 750 K). Recently, a fluoropolymer has been introduced which exhibits many of the desired properties of PTFE and, additionally, is melt processable. This polymer is an alternating semicrys-



1. DATA GRAPHICS MODEL 305 MULTIPLEX SYSTEM
2. DATA GRAPHICS MODEL 509 DIGITAL CLOCK TIMER
3. GENERAL RADIO MODEL 1683 RLC AUTOMATIC BRIDGE
4. DORIC SCIENTIFIC MODEL DS-100 DIGITAL THERMOCOUPLE
5. DELTA DESIGN MODEL 5750 ENVIROMENTAL OVEN
6. TECHTRAN 4100 COMMUNICATIONS TERMINAL

Figure 1. Schematic setup of scanning dielectric instrument.

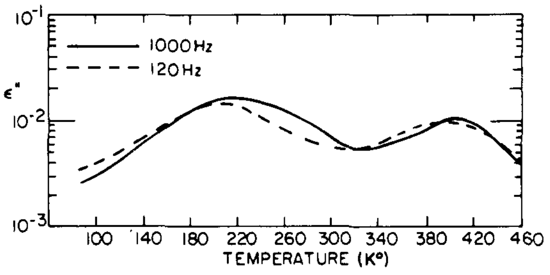


Figure 2. Log ϵ'' vs. temperature for poly(HFIB/VF_2).

talline copolymer of 3,3,3-trifluoro-2-trifluoromethylpropene (hexafluoroisobutylene) and 1,1-difluoroethylene[6] [poly(HFIB/VF_2)]. The dynamic dielectric properties, particularly dissipation factor, are important in such systems. Additionally, the two homopolymers comprising this system should exhibit anomolously low glass transitions[7] which could be due to relatively low energy differences between potential minima of stable rotational conformers of main chain bonds.[8] If this is true, the sub-T_g relaxations of this polymer, as compared with similar symmetrically substituted polymers, might be expected to shed light on the interactions in these systems. Because of these interesting features, the following study has been undertaken.

Experimental Section

The semicrystalline sample of poly(HFIB/VF_2) was provided by Dr. S. Chandrasekaran of Allied Chemical Corp. and is an emulsion polymerized polymer (U.S. Patent 3 706 723). The specimen is birefringent and pseudospherulitic in structure as viewed by polarized light microscopy. The sample is insoluble in common solvents and molecular weight information via GPC or colligative property measurements was unobtainable. Heat pressed films slowly cooled from above T_m as well as melt quenched samples were prepared. For the present studies, the film samples were coated with gold electrodes, mounted in a spring loaded cell, and measured. Dielectric results were obtained in two ways: (1) with an automatic recording dielectric device to ascertain the positions of the relaxations, and (2) with a 1615-A General Radio Bridge with standard accessories to ascertain relaxation time distributions and transition map information.

The automatic set-up has been described briefly elsewhere;[9] however, a more complete description is in order. The schematic set-up for the instrument is shown in Figure 1. Data are obtained by having the Data Graphics Timer/Multiplex system (1 and 2) cue the Doric Digital Thermocouple (4) and General Radio 1683 RLC Bridge (3) at given intervals set by the timer. The timer/multiplex systems were built by Data Graphics Corp., Dallas, Texas, to specifications designed to incorporate the measuring devices into an automatic data acquisition system. The General Radio 1683 RLC bridge is an autoranging instrument capable of measuring capacitance from 0.001 pF to ~2 mF and tan δ from 0.0001 to 1.9999 at frequencies of 120 Hz and 1 kHz. (The capacitance is a function of the frequency with the 1 kHz frequency an order of magnitude better in resolution than 120 Hz.) Dielectric loss can be easily calculated from capacitance and tan δ. The bridge is capable of 20 measurements/s for 1% full scale change at 1 kHz and 2 measurements/s for 1% full scale change at 120 Hz. In the automated mode, the system is limited to readings approximately every second because of limitations of the data acquisition from the 1683 and the DS-100. The bridge operating in a self-triggering mode, rather than remote triggering via the external timer, is capable of the speeds stated above. Data from the bridge are delivered to the Model 305 in terms of five digit capacitance and a five digit tan δ. Range factor for capacitance calculation is also delivered as part of the bridge data. Data from the Doric thermocouple are delivered as a four digit number in Celcius degrees. The B.C.D. data are accepted in parallel and presented sequentially to a magnetic tape recorder. Output code to the tape is ASCII. Thus, at each desired time interval, temperature, capacitance, tan δ and range are recorded on tape. Data are transferred via phone hook-up to a computer, processed, and plotted. Estimated accuracy of tan δ and ϵ'' of the GR-1683 is ±1% of the reading for the present experiment but is, however, a function of the capacitance being measured and is fully described in technical manuals associated with the instrument.

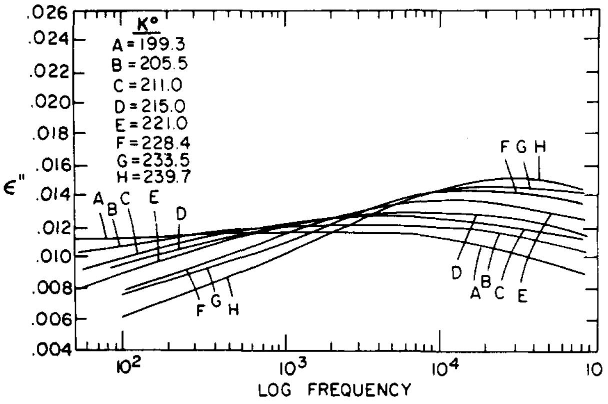


Figure 3. ϵ'' vs. log frequency for the β relaxation in poly(HFIB/VF_2).

Temperature control for the system is with a Delta Design Model 5750 environmental oven. The oven is manually programable, rate programable, and step programable from liquid nitrogen temperatures to ~500 K. The rate program is capable of ~0.1 °C/min to 4 °C/min in the present configuration.

Samples are isolated from the environment in a stainless steel box sealed with Teflon seals (water can be a particular problem in the scanning mode). A thermocouple is mounted through a hole in the box to be within a centimeter of the sample surface. The thermocouple is sealed into the box with epoxy resin. Scanning known samples (polystyrene and polydiancarbonate) indicates that temperature measurement of the samples in this way is accurate to ±2 K at a scan rate of 0.9 K/min. Data for these experiments were recorded with an oven scan rate of 0.9 K/min and data were taken every minute. Data are processed and plotted as ϵ', ϵ'', and tan δ vs. temperature; log ϵ', log ϵ'', and log tan δ vs. temperature; and ϵ'' vs. $1/T$.

Dynamic mechanical measurements were made with a TOYO Model D-II Rheovibron on samples prepared by the quenching technique described above. Calorimetric measurements were made with a Perkin-Elmer DSC-II.

Results and Discussion

A plot of log ϵ'' vs. temperature for poly(HFIB/VF_2) is shown in Figure 2. Two relaxations are observed: a high temperature one near 405 K (designated α) and a low temperature one near 205 K (designated β). These relaxations were investigated dynamically and those results are in Figures 4 and 5.

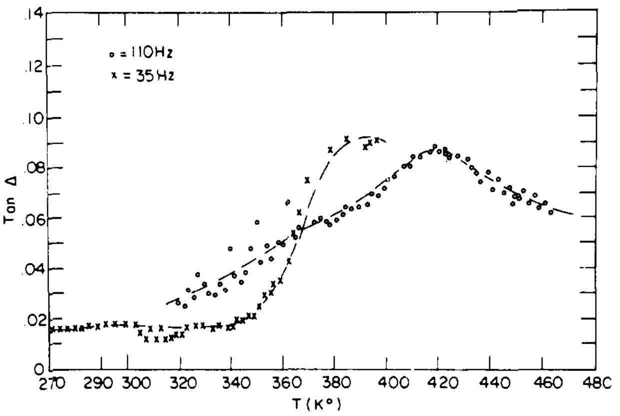


Figure 4. Dynamic mechanical tan Δ vs. temperature at 35 and 110 Hz for poly(HFIB/VF$_2$).

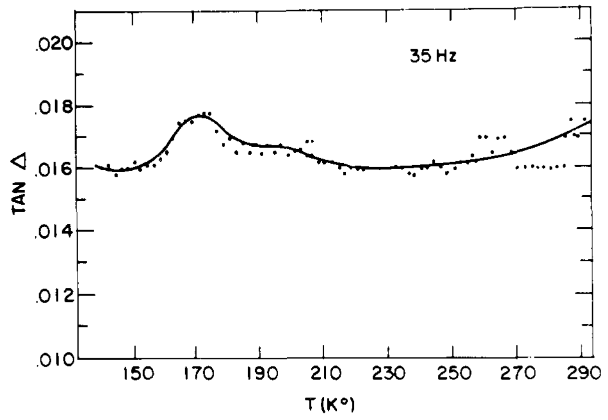


Figure 5. Dynamic mechanical tan Δ vs. temperature at 35 Hz for poly(HFIB/VF$_2$).

A normalized loss plot for the β relaxation is shown in Figure 6. A transition map for the relaxations is shown in Figure 7.

The α Relaxation. The origin of this relaxation is interesting. The crystal melting point has been determined to be 600 K[6] and our value of 603 K measured via D.S.C. verifies that value. Considering frequency factor shifts T_m cannot be the origin of the high-temperature α relaxation. Because of temperature limitations in our device, relaxations that might have been associated with high-temperature crystalline relaxations were not studied. If the standard distribution for T_m and T_g of Lee and Knight[10,11] is applied (i.e., that the most probable value of $T_g \cong 0.66T_m$), a glass transition of 400 K is predicted. This predicted value is very near the observed value for the α relaxation. The α relaxation does not exhibit the characteristic WLF[12] type curve over the observed frequency range in Figure 7 but appears Arrhenius activated with an activation energy of 52 ± 10 kcal/mol.

When the literature is surveyed, it is apparent that adding two substituents in a symmetric fashion to alternating carbons on a polymer chain produces anomalously low values of T_g. This effect has been discussed[13] and typical examples of such behavior are polyisobutylene,[14] polyvinylidene chloride,[15] and polyvinylidene fluoride.[16] In terms of the Gibbs–DiMarzio theory, this low value for T_g can be interpreted in terms of a relatively low energy difference between potential minima of stable rotational conformations of main-chain bonds. Poly(HFIB/VF$_2$) is an alternating copolymer of two monomers which should exhibit the above effect. Unfortunately, poly(trifluoro-2-trifluoromethylproprene) (PHFIB) has not been synthesized and a comparison of the copolymer with this homopolymer cannot be made. Poly(vinylidene fluoride) has a glass transition near −40 °C. If the α relaxation in poly(HFIB/VF$_2$) is T_g and if an equation similar to the Gordon–Taylor equation[18,19] (where the glass transition of the copolymer is an average of the weight fractions of the pure components) could be used in this alternating copolymer system, a glass transition of ~470 K is predicted for PHFIB.

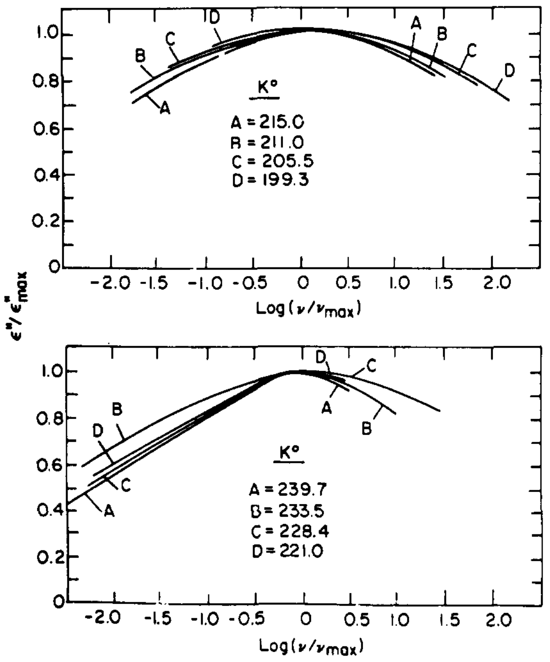


Figure 6. ($\epsilon''/\epsilon''_{max}$) vs. log ($\nu/\nu_{max}$) for poly(HFIB/VF$_2$).

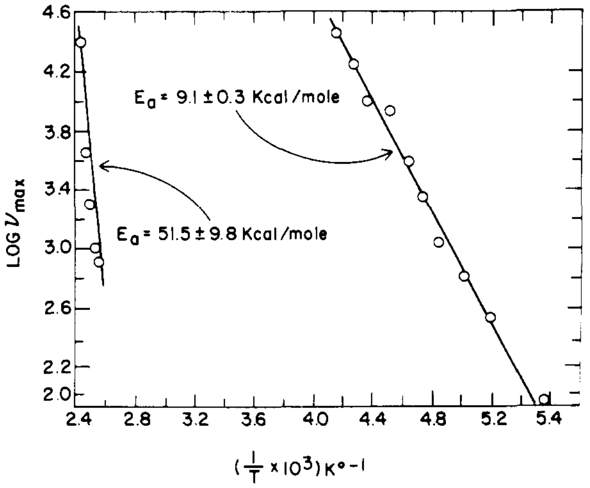


Figure 7. Log ν_{max} vs. inverse temperature for the α and β relaxations in poly(HFIB/VF$_2$).

This value might, at first, be considered highly unlikely. However, in constructing space filling models of poly(HFIB/VF$_2$) it becomes obvious that the polymer must be stiff with motions of the trifluoromethyl group hindered because of the steric size of the fluorine atoms of the adjacent difluoroethylene group, as well as the nearest adjacent trifluoromethyl groups. In fact, it is virtually impossible to make a space filling of PHFIB. A model for poly(HFIB/VF$_2$) shows a rather stiff chain. Polymers with very stiff backbones are expected to have high glass transitions.[8,17,20,21]

On the basis of the high activation energy, the correlation of the α relaxation with the theory of Lee and Knight, and the structure obtained from space filling models, it is concluded that the α relaxation in poly(HFIB/VF$_2$) is the glass transition of the polymer. It has not been possible to verify this assignment via D.S.C. measurements as only a very weak transition near 400 K is observed in a high molecular weight material. No apparent glass transition effect was observed calorimetrically in all other molecular weight poly(HFIB/$\mathrm{VF_2}$) materials studied.[22] Therefore, it is postulated that even though poly(HFIB/$\mathrm{VF_2}$) should structurally produce an anomalously low T_g, the steric hindrance and electronic repulsions of the molecule produce a very stiff chain that exhibits a high T_g (~405 K). In terms of the Gibbs–DiMarzio theory, the high T_g would mean the value of $\epsilon_2 - \epsilon_1$ would be large. Furthermore, if equations similar to the Gordon–Taylor equation can be used in such systems (as is the case for vinyl chloride/vinylidene chloride copolymers[23]) PHFIB may exhibit an exceptionally high glass transition. The same steric problems that would produce the postulated high glass transition probably make synthesis of PHFIB very difficult. Insofar as we can ascertain, this polymer has not been reported in the literature.

The β Relaxation. In terms of the above discussion, the origin of the β relaxation in poly(HFIB/$\mathrm{VF_2}$) is of concern. The β relaxations (the first sub-T_g relaxation) of many halogen containing polymers have been studied.[24–27] In the cases cited, including those for poly(vinylidene fluoride) and poly(vinylidene chloride), the β relaxations are associated with short-range main-chain motion in the amorphous phase and have activation energies of 16 kcal/mol or greater. The value of 9 kcal/mol for poly(HFIB/$\mathrm{VF_2}$) is much lower than those observed in the other fluoro polymers. By analogy, the β relaxation in poly(HFIB/$\mathrm{VF_2}$) is thought to be of an amorphous local nature. The chain stiffness of the polymer is considered to control the energy required for the relaxation to occur. Because of this stiffness, the motion could be of low amplitude which would involve either very short or very long segments of the polymer. In the former case, the trifluoromethyl groups could be considered as semirigid with the $\mathrm{CH_2CF_2CH_2}$ intermediate groups providing most of the motion. In either case, these motions would not be great enough to involve the conformational energy levels involved in the glass transition, but would slightly change the localized conformation of the polymer chain. Thus, although it is postulated that there may be large differences in conformation energy of the polymer for T_g considerations, the conformation energies (or the conformational barriers between them) for the low amplitude motions must be small. The normalized plot of the relaxation shown in Figure 6 would indicate that the distribution of relaxation times for the β relaxation is narrowing with increasing temperature.

In an attempt to verify our assignment of the β relaxation, quenching experiments to alter the degree of crystallinity were conducted. All attempts to quench the polymer from above T_m to liquid nitrogen temperature and ice/water slush temperatures resulted in samples morphologically and dielectrically indistinguishable from their slow cooled counterparts. Density measurements to determine the degree of crystallinity were invalid due to the inclusion of small bubbles in both quenched and original films.

Thus, although the β relaxation is postulated to arise from the amorphous segments of the system, this hypothesis cannot be verified at this time. Figure 5 also provides hints of an additional relaxation in the temperature region above the β relaxation. However, the tan δ's measured are near the ultimate resolution values attainable in our Rheovibron so the additional relaxation must be viewed with skepticism until it can be further verified. Dielectric techniques did not show the relaxation.

In summary, the α and β dielectric relaxations for an alternating copolymer of poly(HFIB/$\mathrm{VF_2}$) have been studied. It is proposed that these relaxations are the glass transition and local mode motion of the polymer chain, respectively. The relatively high value of T_g (~405 K at 120 Hz) is discussed in terms of chain stiffness due to steric interactions and electronic repulsion. It is postulated that poly(3,3,3-trifluoro-2-trifluoromethylpropene), if it could be synthesized, would possess an exceptionally high T_g because of these same effects. The β relaxation is assigned to low-amplitude motions of the main chain. Because of these interesting results, the polymer is also being studied via pulsed NMR techniques to see if the mechanisms proposed for the α and β relaxations can be further elucidated.

Acknowledgment. The authors wish to thank D. Tasseff for her typing. Samples of poly(HFIB/$\mathrm{VF_2}$) were graciously supplied by Dr. S. Chandrasekaran and Dr. M. Meuller of the Allied Chemical Corp.

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