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The dielectric relaxation behavior of semi crystalline poly(tetrahydrofuran) networks

A.A.F.Zikry[1], M.T.El-Hefnawy[2], H.M.A.Ahmed[1,2], M.A.Sharaf[1]*

[1]Department of Chemistry, Helwan University, Ain Helwan, Cairo 11795, (EGYPT)

[2]Department of Chemistry, College of Engineering, Benha University at Shubra, Cairo, (EGYPT)

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ABSTRACT

The dielectric relaxation behavior of hydroxyl-terminated poly tetrahydrofuran (HO-PTHF-OH) network has been investigated.The networks were prepared by a hydrolysis condensation process of the 3-isocyanato propyltriethoxysilane end capped-oligmers for the crystalline relaxation covering a range in the temperature and frequency. Also, the crystallization process of the investigated sample has been studied dielectrically as a function of time and temperature. Furthermore, the results obtained showed that (i) the optimum crystallization temperature is about 25^{0}C; (ii) the time at which crystallization starts is a function of the working temperatures and apparently is reduced to just a few minutes at 30^{0}C; and (iii) the crystallization process is completed within a period of less than 1 hrs in the temperature range 20-30^{0}C.

INTRODUCTION

Polymer systems may exhibit a rich hierarchical structure when crystallize at temperature above the glass transition temperature(T_g). The process of crystallization has been historically studied from the viewpoint of the crystalline structure development[1]. However, polymers never crystallize completely and they always present a complex structure, consisting, at least, of two phases: crystalline and amorphous.

The molecular motions occurring in the amorphous phase of a semicrystalline polymer present characteristic aspects which depend, in a first approximation, on the degree of crystallinity[2]. In semicrystalline polymers at temperatures higher than the glass transition temperature, T_g, the amorphous polymer chains are confined to move between the crystalline regions[2-4]. This restriction modifies the dielectric α relaxation which is detected in polymeric systems at temperature above T_g. It is known that this relaxation involves motions extended to several molecular segments. However, when dealing with the dynamics of the amorphous phase in a semicrystalline polymer, the crystallinity itself is not enough to characterize the system, and profound information about the microstructure, i.e., this crystallinity is distributed along the sample, is needed. Crystallization at conditions of relatively high chain mobility and low nucleation density leads to a morphology that imposes less constraint on the motion of the amorphous chains. That loosening of the crystalline constraint has been attributed to improved crystal perfection i.e., a decrease in lamellar surface roughness[5] as well as a thickening of the amorphous interlayer[6,7]. Dielectric relaxation spectroscopy is a powerful technique that can detect the molecular dynamics as well as the transformation phenomena in polymers at the earlier stages.

Dielectric spectroscopy(DS) techniques are widely used to study the dynamic of the amorphous chains in polymeric systems[8]. DS has been used to study, in real time, the modification of the dynamics of the segments in the amorphous phase during crystallization processes[9].

The α relaxation, that appears at T>Tg associated to the segmental motions of the chains in the amorphous state. This α relaxation is highly affected by crystallization process.

The dielectric relaxation characteristics of amorphous and semicrystalline poly (ether ether ketone) have been investigated as a function of crystallization history; both the α-relaxation and β-relaxation were examined[10]. The characteristics of the α-relaxation were highly sensitive to crystallinity owing to the constraint imposed on the amorphous phase dipoles by the presence of the crystalline phase. The magnitude of the α-relaxation strength indicated an immobilized rigid amorphous phase fraction in the semicrystalline samples which appeared to relax at temperature above T_g; finite rigid amorphous fractions were observed for both cold-crystallized and melt-crystallized specimens. The β relaxation was also sensitive to the presence of crystallinity: the isochronal loss maxima measured for the cold-crystallized samples were offset to higher temperature as compared to the wholly-amorphous material, and a disproportionate decrease in the β strength with the degree of crystallinity was observed. The influence of the crystalline phase on the β relaxation thus appears to extend well into the amorphous material length scale as compared to more flexible polymers.

In this study, the dielectric relaxation characteristic of a series of semicrystalline hydroxyl-terminated polytetrahydrofurane network (OH-PTHF-OH) is investigated. The crystallization process is studied as function in the dielectric relaxation spectroscopy (DRS). Also we study the time at which the crystallization starts as a function of the working temperature.

EXPERIMENTAL

Materials

Tetrahydrofuran(THF) was obtained from the Fischer Company as HPLC grade and then distilled over potassium metal. Trifluromethanesulfonic acid anhydride(triflic anhydride) was used as received from the Aldrich Company, and sodium hydroxide and diethyl ether were similarly used without further purification. 3-isocyanatopropyltriethoxysilane(95%) was purchased from United Chemical Technologies, Inc. Stannous octoate was obtained from Pfaltz & Bauer, Inc. and used without further purification. For purposes of comparison, two low molecular weight PTHF samples were obtained from the Aldrich Chemical Company, with quoted number average molecular weights of 650 and 2,900g mol^{-1}.

Synthesis of hydroxyl-terminated polymer

Tetrahydrofuran(THF) was polymerized by a cationic ring opening mechanism[11]. The details of the procedures of synthesis are as follows: 2.5ml of triflic anhydride was added to 200ml of distilled THF. The mixture was mechanically stirred at -5^0C for 90min and the polymerization permitted to proceed under an inert atmosphere (dry Ar). 20ml of 3% aqueous NaOH solution was added to the polymer thus formed, and the mixture was then stirred for 30 min at 0 ^{o}C. This gave hydroxyl-terminated polymer[11].

Synthesis of the elastomeric networks

The PTHF networks were prepared in a previous study[11] by end-capping the hydroxyl-terminated PTHF with 3-isocyanatopropyltriethoxysilane, using Sn-octoate (tin-2 ethyl hexanoate) as catalyst Under an Ar atmosphere, the polymer was dissolved in anhydrous THF and stirred continuously at 60^0C, after which Sn-octoate(1.2% of the weight of polymer) was added and the stirring continued for 10min[11]. A stoichiometric amount of 3-isocyanatopropyltriethoxysilane was added with continuous stirring for 10min at the same temperature. Some additional formulations were made with stoichiometric imbalance, with the compositions characterized by the molar ratio r≡[end linker]/[polymer][11]. The reaction mixture was poured into an aluminum mold, subsequently sealed with Teflon, and the reaction carried out on a hot press at 70-80^0C for 24-30hrs. The resulting networks were extracted with toluene at room temperature, gradually deswelled with methanol, and then dried in a vacuum oven for two days.

Characterization of the oligomers and networks

The hydroxyl-terminated polytetrahydrofuran were synthesized in a previous study[11]. The oligomers thus obtained were characterized using gel permeation chromatography(Waters GPC model 501) with toluene as solvent, and with polystyrene standards. Infrared measurements were carried out using a Perkin Elmer (Spectrum one) Spectrophotometer[11].

Differential scanning calorimetry DSC experiments were carried out with a Perkin-Elmer DSC_7 instrument at a heating rate 10^0C/min. Sub-ambient operation was carried out by using a controlled flow of cooled nitrogen gas by using a Perkin-Elmer TA7. The temperature was calibrated by using indium standard. The samples were encapsulated in aluminum pans and the typical samples weights used in these experiments were about 5mg. In differential scanning calorimetry(DSC), the thermal properties of a sample are compared against a standard reference material which has no transition in the temperature range of interest, such as powdered alumina.

Dielectric spectroscopy measurements

The dielectric constant and dielectric loss were measured using HIOKI(3532) LCR type which has a frequency band from 42Hz to 5MHz with high resolution. This device is an impedance meter, uses a touch panel which enables easy operation.

The dielectric sample is subjected to an alternating electric field. The sample is usually a thin disc prepared by molding, calendaring, or solvent casting. To insure good contact with the electrodes of the condenser, the sample must have thin electrodes adhered directly to its surfaces. These electrodes can be vacuum deposited, painted with special conducting paints containing colloidal silver or graphite, or made of aluminum foil carefully oiled in place.

The measurements monitored using thin samples prepared in the form of discs 10mm in diameter and 1.4mm thick by using (HIOKI LCR 3532) type with a dielectric interface and control temperature unit in frequency range 1×10^3-5×10^6 at different temperatures.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC)

The network investigated here had Mm=2900 and r=1.In figure 1 the Differential Scanning Calorimetry (DSC) for the investigated sample is illustrated. It can be seen that, there is a sharp peak at about 50^0C and a set of multiple peaks of lower intensities in the temperature range to. This could be owing to higher values of the polydispersity index of network chains.

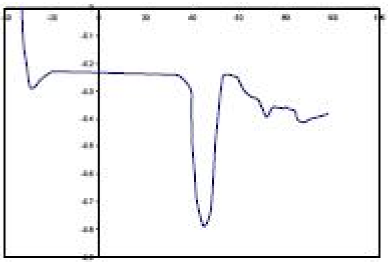

Figure 1 : Differential scanning calorimetry of HO-PTHF-OH network

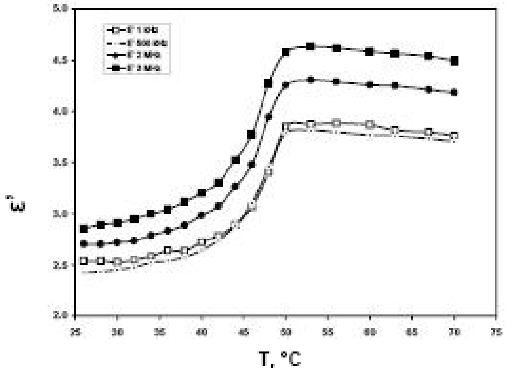

Figure 2 : Variation of dielectric constant (ε') with temperature at different frequency

Dielectric measurements

Dielectric results for OH-PTHF-OH network are presented as plots of dielectric constant, ε', and dielectric loss, ε'', versus temperature at different frequency.

The variation of dielectric constant, ε', with temperature at different frequencies is shown in figure 2. It is evident from this figure that a stepwise increase in ε', with temperature due to an increase in the effect of mobility, that leads to an increase in the orientation polarization and hence an increase in ε'. The increase in moblities would also enhance, the ease of rotation and polarization of the side groups and other flexible portions of the polymer chain.

The stepwise increase in ε' corresponds to large scale mobilization of the amorphous chains present. An increase in temperature past the melting transition of the investigated sample, the values of dielectric ε' reaches its maximum value and a plateau is attained afterwards.

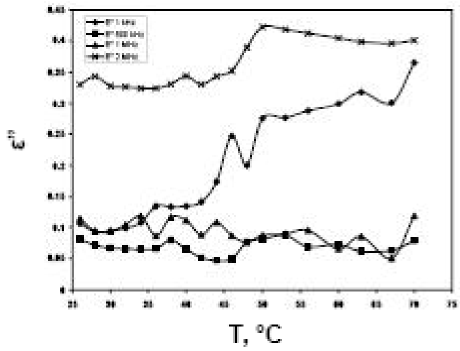

Figure 3 : Variation of dielectric loss (ε'') with temperature at different frequency

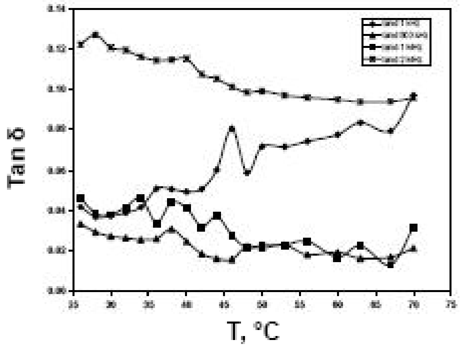

Figure 4 : Variation of loss factor (tanδ) with temperature at different frequency

The shape of dielectric constant versus temperature curve past the melting transition is determined by two factors. Namely, the temperature changes induced in film thickness, and the conversion of semicrystalline to amorphous material. The maxima in ε' (t) is an evidence of melting liquid relaxation. In most of practical applications, the dielectric constant of the materials used for capacitors should be stable within the operational temperature range of electronic devices[12].

The variation of dielectric loss, ε'', of HO-PTHF-OH networks with temperature at various frequencies is shown in figure 3. It can be seen that, an increase in dielectric loss, ε'', with temperature occurs due to the enhanced orientation of possible polarization in the system. A multiple set of melting transition peaks that are frequency dependent is observed. This is in agreement with the DSC results, cf. figure 1. This behavior is certainly owing to high polydispersity of the oligomer and to imperfection in the formation of the network by sol gel condensation that could result in a fraction of the chains highly constrained by crosslinks of higher functionalities[11]. Undoubtedly a fraction of the chains would be unrestricted owing to inexact stoichiometry. Thus, as would be expected, crystallites having different sizes and constraints on their cooperative motion will be present. Such behavior would be reflected in the presence of the observed multiple transitions.

It is known universally that, there are two types of dielectric loss for all polymers[13]. The first type of dielectric loss is called dipole segmental loss which associated with orientational rotation of the polar units of the macromolecule under the conditions where segmental movement is possible. The relaxation of crystalline chains observed in figures 2 and 3 is attributed to crystalline-amorphous transitions that would be owing to increased segmental motions taking place in the amorphous phase at temperatures above the T_m. The second type, called dipole group, is due to orientation of the polar groups themselves. This relaxation observed is attributed to the melting of the crystalline domains. Subsequently, the mobility of the amorphous chains and orientation of dipoles will increase; as is clearly indicated by the apparent increase in έ.Again in figure 4, the multiple relaxations are shown in the plot of tanδ vs. temperature. One again, the results are in excellent agreement with results obtained from DSC measurements.

The relaxation in polymer was described by means of Havriliak-Negami (HN) equation[14] empirical relaxation function:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(i\omega\tau)^b]^c} \qquad (1)$$

where ε is the complex dielectric permittivity, ε* = ε'-iε'', ε and ε∞ being the relaxed and unrelaxed dielectric constant values T is the central relaxation time of the relaxation time distribution, and b and c (0<b, c<1) are shape parameters which describe the symmetric and asymmetric broadening of the relaxation time distribution function, respectively. When b=1, Equation (1) reduces to Davidson-Cole expression corresponding to a relaxation spectrum which is skewed to higher frequencies, while for c=1, Equation (1) leads to Cole-Cole function[15] corresponding to a broad but symmetric relaxation curve. When both b and c are equal to the unity, the Debye expression is recovered.

Argand diagrams of dielectric loss, ε'', versus dielectric constant, ε', were constructed at some selected

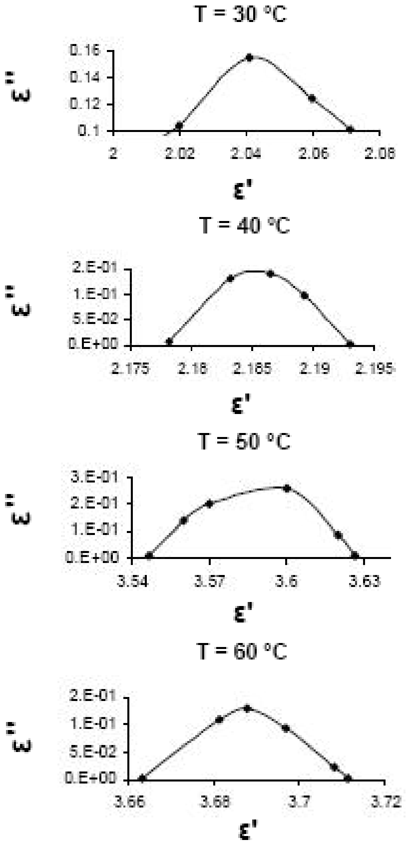

Figure 5 : Argand diagram of HO-PTHF-OH network

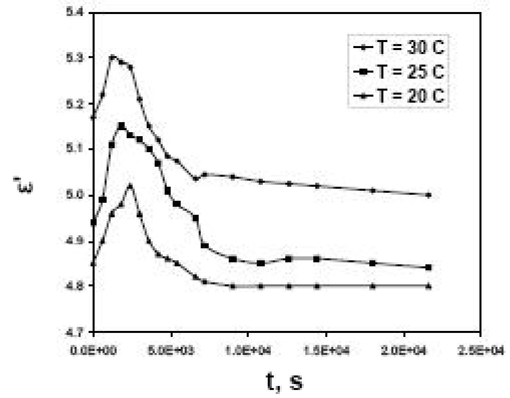

Figure 6 : Dielectric constant, (ε'), as a function of time at different crystallization temperatures

temperatures for OH-PTHF-OH network samples; representative results for samples are shown in figure 5. It can be noticed that, the dispersion was symmetric and was described by Cole-Cole form of Havriliak-Negami (HN) equation with a, the skewing parameter, equal to unity. In Cole–Cole plots, the plot is perfect semicircle with the center on the axis of dielectric constant, so a primary single relaxation time describes the materials.

Similarly, in totally amorphous polymer, the glass transition process studied dielectrically has a loss peak or complex plane plot that is skewed toward high frequency but is otherwise relatively narrow[16]. In contrast, in semicrystalline polymers, the process appears to be more symmetrical and much broader.

One particularly intriguing aspect of dielectric spectroscopy is its applicability to the studies of systems that undergo chemical and/or physical changes during the application of the electric field, due to, for example, chemical reactions or crystallization[2]. The latter situation is addressed in this communication. Specifically we show how one can follow by dielectric measurements the two principal polarization mechanisms in organic dielectric materials, namely charge migration and dipole orientation, and utilize them to monitor the development of crystallinity and morphology.

In this investigation, we have probed the use of dipoles as molecular probes in the study of the crystallization kinetics are very attractive because it provides a direct measure of the chemical and physical state of the matter in real time. The reorientational dynamics of the dipoles can be investigated by dielectric measurements in the desired frequency, time, and temperature domain.

In figure the onset of crystallization at 25^{0}C, following the induction period of 40 minutes, brings about a dramatic change in the dielectric response. This is clearly seen in figure 6 where dielectric constant is plotted as a function of time with temperature as a parameter. This figure shows gradual increase in the peak intensity as a result of isothermal crystallization.

The figure shows also how the peak intensity decreases with time as a result of the ongoing crystallization. In other words, the observed drop in the dielectric constant during crystallization is caused by the transformation of the amorphous phase into a crystalline one, whereby the reorientational ability of dipoles is drastically reduced.

The optimum crystallization temperature can be evaluated experimentally using the traditional method. This can be done by scanning the dielectric constant at different crystallization temperatures(25, 30 and 40^{0}C) as a function of time, as shown in figure 6. This figure shows that the dielectric constant increases during the first few minutes of measurement. The increase can be attributed either to an increase in the sample tempera-

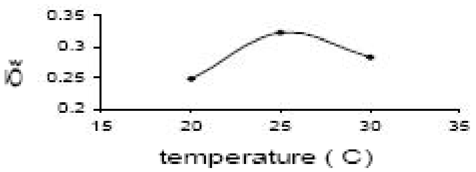

Figure 7 : Dielectric constant decrement,(δε), as a function of crystallization temperature (T_c)

ture to attain a pre-ordered state that is required for achieving the crystallization process. However, due to the extremely small weight of the sample(0.1g) which is placed between two copper electrodes(thermally conducting) and mounted in a preheated measuring cell with a homogenous heating flux, it is impossible to attribute this increase to the attainment of thermal equilibrium. Therefore, it can be concluded that the increase in ε' is mainly attributed to a pre-order reorientation process of the dipoles. This process is followed by the crystallization process which strongly restricts the dipolar reorientation and therefore leads to a rapid decrease in the dielectric constant. It would be expected that an increase in the temperature would lead to a faster preorder process. This implies that the onset time at which the crystallization process starts will be shorter with increasing temperature, since the onset crystallization time is shortened from 40 min to 30 and 20 for 25, 30 and 40^0C, respectively.

It can be expected that, a plot of the decrement in the dielectric constant, δε, with the crystallization temperature figure 7 would offer a possibility for determining the optimum crystallization temperature, $T_{C(max)}$, where δε is the difference between the dielectric constant at the onset time of crystallization and that after attaining equilibrium[17]. Figure 7 Shows that the optimum crystallization process is around 25^0C. The molecular motions occurring in the amorphous phase of a semicrystalline polymer present characteristic aspects which depend on the degree of crystallinity[18]. In semicrystalline polymers, at temperatures higher than the glass transition temperature, T_g, the amorphous polymer chains are confined to move between the crystalline regions[4]. This restriction modifies the dielectric α relaxation which is detected in polymeric systems at temperatures above to T_g. The observed decrease in the rate of crystallization is common for semi crystalline polymer; at lower crystallization temperature is expected owing to lower chain mobilities.

ACKNOWLEDGMENTS

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