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Polymer 40 (1999) 5961–5965

polymer

Polymer Communication

The influence of vinylidenefluoride on the free volume of poly(chlorotrifluoroethylene)

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Received 30 November 1998; received in revised form 18 February 1999; accepted 1 March 1999

Abstract

The influence of vinylidenefluoride (three different compositions, viz. 0, 0.5 and 3.0%) on the free volume of the polymer poly(chlorotrifluoroethylene) has been investigated using the Positron Annihilation Lifetime technique. The lifetime results indicate that, with the increase in the composition of vinylidenefluoride, the average free volume size of the polymer decreases whereas their number density increases. Further, it has been observed that the glass transition temperature (T_g) of this polymer decreases with the increase in vinylidenefluoride content. The present results complement the literature report that vinylidenefluoride influences mainly the amorphous regions of poly (chlorotrifluoroethylene).

Keywords: Positron annihilation lifetime technique; Vinylidenefluoride; Poly(chlorotrifluoroethylene)

1. Introduction

It is common in polymer chemistry to modify the properties of a homopolymer by the introduction of a second monomer in a suitable proportion resulting in a copolymer with properties intermediate between those of the parent homopolymers [1]. This copolymerization permits the synthesis of an almost unlimited range of polymers and is often used, therefore, to obtain a better balance of properties for commercial application of polymeric materials. It has been noted that although the homopolymers are immiscible with other polymers, the copolymers are more likely to be miscible in them [1]. For example, neither polyethylene nor poly(vinylacetate) is miscible with poly(vinylchloride) whereas some ethylene/vinyl acetate copolymers are miscible. The miscibility will reduce the number of unfavourable contacts between the two types of segments [1]. Another advantage of copolymerization is that one can improve upon the mechanical, electrical and optical properties of the product [2].

Further, the process of copolymerization is one of the ways of increasing the amorphous content of a polymer. This is because, copolymerization introduces units that destroy the regularity of the chains and hence the tendency to pack together in the crystalline form decreases [3]. The decrease in crystallinity leads to reduction in stiffness, hardness and softening point [4]. Also, copolymerization may improve the polymer characteristics such as yield strength, specific gravity, impact strength and the stability to overcome the degradation effects from agencies such as thermal, photochemical and high energy radiations [5].

In the amorphous regions of a polymer, there exits certain low electron density regions called the free volume holes. In recent years, it has been shown that free volume can be treated as an internal material parameter based on which the visco-elastic properties of the polymers can be understood. Of the different techniques, the Positron Annihilation Lifetime (PAL) technique is a novel tool for characterizing these free volume holes as it measures both the average free volume size and their population [6,7]. This is based on the fact that the ortho Positronium (o-Ps) is formed and annihilated mainly in these free volume sites [8]. For details on positron and positronium decay in polymers, one can refer to the articles by Stevens [9] and Jean [7].

Of particular interest, is the polymer, poly(chlorotrifluoroethylene)—PCTFE. It has been observed that the addition of vinylidenefluoride (VF_2) as a comonomer to PCTFE enhances the thermal, chemical and mechanical properties of the latter [10]. Furthermore, the increase in the amorphous content of PCTFE with the addition of VF_2 has

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0032-3861/99/$ - see front matter
PII: S0032-3861(99)00165-2

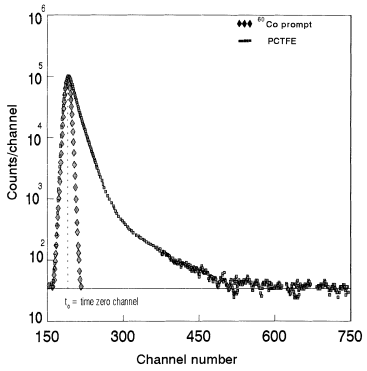

Fig. 1. Typical lifetime spectrum of PCTFE with ^{60}Co prompt spectrum.

been reported [10,11]. More amorphous content in turn leads to high impact strength in this polymer. A change in the amorphous content may indicate a change in the free volume content, hence it is interesting to study the free volume behaviour in a polymer with various compositions of a copolymer. Additionally, it is of interest to understand the site of localization of VF_2 in the PCTFE structure. To understand these aspects, we have measured the average free volume hole size and their number density in PCTFE as a function of VF_2 concentration using the PAL technique.

2. Experimental

The PCTFE films used in this study are marketed by Allied Signal Inc., USA as 'Aclar'. The sample with 0% VF_2 is denoted as HP, that with 0.5% VF_2 as TVS and that with 3.0% VF_2 as 22A. The weight average molecular weight of these samples (films) is 250 000. The films were cut into two equal parts and approximately 1 mm of the films were stacked to form two identical samples. A 15 μCi ^{22}Na positron source deposited and sealed on a kapton foil of 0.0127 mm thickness was sandwiched between the aforesaid two identically stacked samples (12 films each of thickness 0.076 mm in case of 22A, six films each of thickness 0.2 mm in case of TVS and three films each of thickness 0.4 mm in case of HP) to form a source sample sandwich for positron lifetime measurements. They were placed between the two detectors of the lifetime spectrometer. The positron lifetime spectrometer consists of a fast–fast coincidence system with a time resolution of 340 ps. The details of the spectrometer can be found elsewhere [12,13]. More than one million counts were collected for each spectrum at room temperature. The experiment was repeated for each sample to check the reproducibility of the measurements and consistently reproducible spectra were used in the final analysis. The source correction term and the resolution function were obtained from a metal spectrum of known lifetime (well-annealed aluminium) using the program RESOLUTION [14]. The measured lifetime spectra were analysed using the program PATFIT-88 [14].

3. Results and discussion

A typical lifetime spectrum of PCTFE along with the ^{60}Co prompt spectrum is presented in Fig. 1. All the positron lifetime spectra were analysed into two, three and four components. The three-component fit gave better χ^2 values and standard deviations than the two- and four-component fits. In the three-component fit, the intensity of the third component (I_3), although small (2.5–4.5%) is considered, because the four-component fit gave negative intensities and higher χ^2 values. Hence, the three-component fit lifetime results are presented and discussed here. In general, compared to other polymers, the fluoropolymers are known to have lower o-Ps intensity (I_3) [15]. This suggests that in PCTFE, the free volume distribution comprises a small number of large holes. Because of the low I_3 value, the source correction term was carefully measured and it was found that it contained no term having a lifetime around the τ_3 value reported here.

The attribution of the three lifetimes to various states of positron annihilation are as follows: the first short lived component τ_1 with intensity I_1 is attributed to *p*-Ps and free annihilations. With regard to the attribution of the second or the intermediate lifetime component (τ_2) and its intensity I_2, there is some ambiguity, since different research groups follow slightly different approaches. We follow the prescription outlined by Goldanskii et al. [16] according to which the intermediate lifetime component (τ_2) with intensity I_2 is considered to be caused due to annihilation of positrons trapped at the defects present in the crystalline regions or trapped at the crystalline–amorphous (c–a) interfaces. The longest lived component τ_3 with intensity I_3 is attributed to pick-off annihilation of the o-Ps in the free volume sites [7,13].

The annihilation of o-Ps in the free volume sites can be described by a simple quantum mechanical model [17–19]. As per this model, the positronium is assumed to be localized in a spherical potential well with an electron layer of thickness ΔR and the relationship between the radius R of the free volume hole and the o-Ps lifetime (τ_3) is

$$1/\tau_3 = 2[1 - (R/R_0) + (1/2\pi)\sin(2\pi R/R_0)] \quad (1)$$

with $R_0 = R + \Delta R$ and the reasonable assumption that the lifetime of the o-Ps in the electron layer is the spin averaged Ps lifetime of 0.5 ns. The value of $\Delta R = 0.1656$ nm was determined by fitting Eq. (1) with experimental τ_3 values and the known hole radii for molecular materials. Using this value of ΔR, the free volume radius R was evaluated from Eq. (1) and then the free volume size (V_{f3}) was calculated as $V_{f3} = 4/3(\pi R^3)$. The fractional free volume (F_v) can be estimated as

$$F_v = CV_{f3}I_3 \quad (2)$$

in which C is the structural constant. One way of calculating C is from a measurement of the thermal expansion coefficient of the free volume (α_0). This α_0 is calculated using the

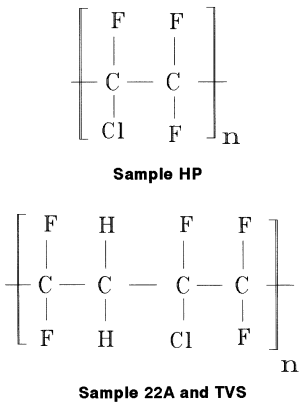

Fig. 2. Chemical structure of PCTFE homopolymer (HP) and with VF_2 comonomer added (TVS and 22A).

value of V_{f3} obtained through Eq. (1) as follows:

$$\alpha_0 = (V_{f3T} - V_{f30})/V_{f30}(T - T_0) \qquad (K^{-1}), \tag{3}$$

where V_{f30} and V_{f3T} are the sizes of the free volume at room temperature and at a temperature where the free volume expansion is maximum (this was done in a separate isochronal annealing experiment in which the free volume radius and its size were calculated at each annealing temperature. The results are not reported here). T_0 and T are the corresponding temperatures. The value of α_0 for 22A, TVS and HP turns out to be 3.603×10^{-3}, 2.907×10^{-3} and $0.9282 \times 10^{-3}\ K^{-1}$, respectively, which is in agreement with the polymer data available. Based on the Williams, Landel and Ferry (WLF) theory [20], the fractional free volume (F_v) can be represented as [21]

$$F_v = 0.025 + \alpha_0(T - T_g). \tag{4}$$

Now using the value of α_0 obtained as described above, Eq. (4) is fitted for temperatures from T_g to (T_g + 100 K). The value of F_v so obtained at each temperature is used in Eq. (2) to calculate the value of C since we know V_{f3} and I_3 at these temperatures. In this way we obtain the value of C as

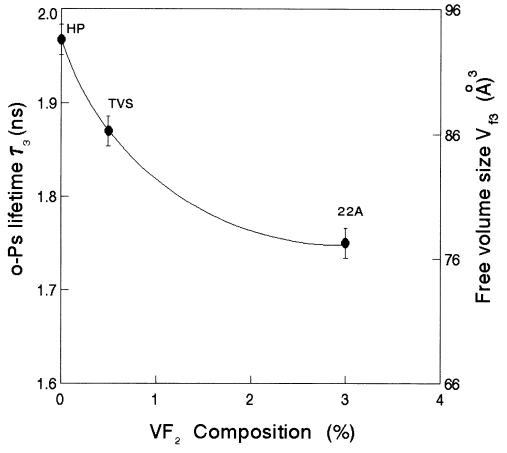

Fig. 3. Variation of o-Ps lifetime (τ_3) and free volume size (V_{f3}) as a function of VF_2 composition (the line drawn is a guide to the eye).

0.0065, 0.0105 and 0.0116 $Å^{-3}$ for 22A, TVS and HP respectively. We have estimated the C value in the range T_g to (T_g + 100 K), where the WLF theory and hence, the temperature dependence of the fractional free volume (Eq. (4)) are valid [22]. These values of the structural constants were used in the present experiment to calculate F_v.

The change in the value of the structural constant clearly points that the structure of the polymer gets altered upon VF_2 addition. The structural constant decreases with increase of VF_2 content. The percentage change in the value of C is 12% for 0.5% addition of VF_2 and 45% for a mere 3% addition of VF_2. The glass transition (T_g) of these three polymers are found from a separate isochronal annealing experiment from the plot of lifetime parameters vs. annealing temperature and the details of the experiment are reported elsewhere [13,23]. The T_g values for 22A, TVS and HP are 52, 62 and 70°C respectively and these values are in good agreement with the DSC measurements.

The chemical structures of PCTFE with the absence and presence of VF_2 are shown Fig. 2. The variation of o-Ps lifetime (τ_3) and the free volume size (V_{f3}) as a function of VF_2 composition are depicted in Fig. 3. The V_{f3} and hence the τ_3 value decreases gradually with VF_2 composition. Fig. 4 presents the variation of the o-Ps intensity (I_3) and the fractional free volume (F_v) as a function of VF_2 composition. Further, the plot of the glass transition temperature (T_g) against VF_2 composition is presented in Fig. 5. It is clear from this figure that T_g shows a decreasing trend with the increase in VF_2 composition.

In the structure of PCTFE (see Fig. 2), the skeletal angles on the two backbone forming carbon atoms CF_2 and CFCl cannot be equal because of the difference in size of the F and Cl atoms. Consequently, the presence of two alternating unequal angles within the polymer chain backbone cannot be accommodated in a planar arrangement of the chain backbone or in an arrangement in which the atoms of the backbone would lie at equal distances from the axis of the helix [24]. The most acceptable shape of the polymer chain seems to be a corkscrew shape in which the two carbon atoms lie at different distances from the helix axis and winds around it [25]. A suggestion was made that this may represent a twisted ribbon like structure analogous to that proposed for banded spherulites of polyethylene and other polymers [26]. X-ray powder pattern of the CTFE–VF_2 equimolar structure suggests a fair amount of disorder along the chain direction. This may be interpreted as an indication of randomness in the positions of the chlorine atoms along the chain of one-to-one copolymer. This points to a constitutionally irregular system containing head-to-head ($-CH_2-CF_2-CClF-CF_2-$) and head-to-tail ($-CF_2-CH_2-CClF-CF_2-$) sequences or a low degree of alternation [10]. But, NMR study excludes the presence of head-to-head structure [27] and therefore, the most probable structure is head-to-tail. Due to the asymmetry in the size of F and Cl atoms, the structure of CF_2 and CFCl would be different and it is a probable site where the chain can fold

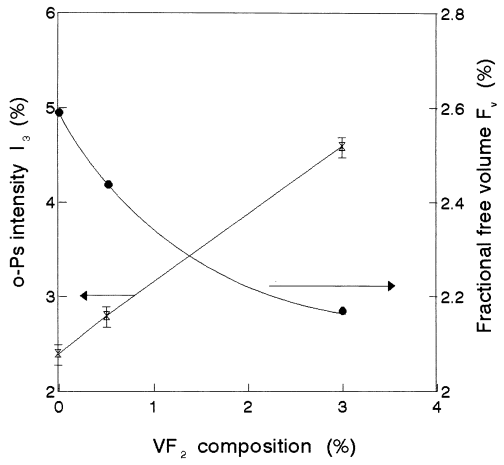

Fig. 4. Variation of the o-Ps intensity (I_3) and the fractional free volume (F_v) as a function of VF_2 composition (the line drawn is a guide to the eye).

to a greater extent resulting in the formation of additional free volume sites.

The decrease in the average free volume size (V_{f3}) and the increase in o-Ps intensity (I_3) (see Figs. 3 and 4) can be explained in the following way: Inhibition and anti-inhibition of positronium (Ps) formation in different molecular media in the presence and absence of additives have been described by several investigations [28–31]. If Ps formation is inhibited, it is normally seen as a decrease in o-Ps intensity whereas quenching of o-Ps leads to decrease in o-Ps lifetime (τ_3). The supporting evidence can be found in the earlier works like the following: Halogenated compounds are the best examples for these observations. It has been found that in the presence of C_6F_6 additive, halogenated compounds have shown increase in o-Ps intensity indicating that the C_6F_6 additive acts as an anti-inhibitor of *p*-Ps [29]. Some halogenated compounds on addition of nitro compounds show great reduction in the o-Ps intensity. It was also found that the inhibiting effect seems to depend on the chlorine position in the polymer structure. In the light

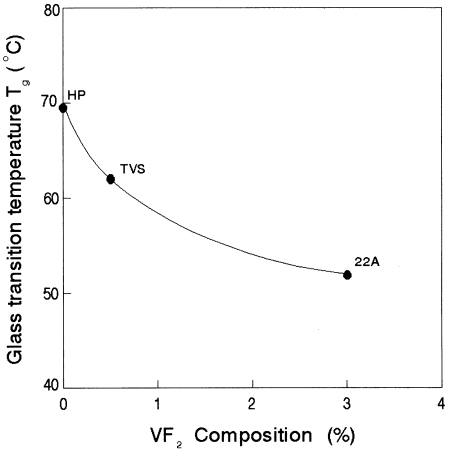

Fig. 5. Variation of the glass transition temperature (T_g) as a function of VF_2 composition (the line drawn is a guide to the eye).

of these observations, the linear increase in o-Ps intensity (I_3) in the present data can be termed as due to the anti-inhibiting effect of VF_2. But, the decrease in τ_3 and hence the free volume size may be due to the localization of VF_2 in the free volume cavities which is in agreement with earlier results [10,32]. Even the fractional free volume (F_v) or the total free volume content in the sample decreases.

As stated earlier, the addition of the VF_2 comonomer also leads to an increase in the amorphous content of PCTFE [10,32] since the former destroys the regularity of the chains in the latter. Once the amorphous content of the sample increases, one expects the number of free volume sites to increase. This is reflected in Fig. 4.

It is evident from Fig. 5 that the T_g values of PCTFE decreases with the increase in VF_2 composition. This means that the VF_2 addition results in an increase in the amorphous content of the polymer. Owing to this change in amorphous content, the T_g, which is the effective temperature at which the polymer becomes rubbery decreases as evidenced by the variation of T_g with VF_2 composition in Fig. 5.

4. Conclusions

The effect of VF_2 on the free volume of PCTFE has been probed using the PAL technique. The present study reveals that VF_2 acts as an anti-inhibitor of *p*-Ps formation and localizes mainly in the free volume sites of PCTFE. The addition of VF_2 results in an increase in the amorphous content of PCTFE.

Acknowledgements

The authors are thankful to Dr N.S. Murthy (Allied Signal Inc., NJ, USA) for providing the PCTFE samples. Five of us (P.R., G.R., G.S., M.C.T. and P.M.S.) are grateful to the University of Mysore, Mysore for providing the facilities for this research at the Department of Studies in Physics, Manasagangotri, Mysore 570 006.

References

[1] Comprehensive polymer science, 2 and 3. New York: Pergamon, 1989.
[2] Agarwal JP. Composite materials. New Delhi: Defence Scientific Information and Documentation Centre, 1990.
[3] Bawn CEH. The chemistry of high polymers. London: Butterworths, 1948:210.
[4] Billmeyer FW. The text book of polymer science. 3. New York: Wiley, 1994.
[5] Brydson JA. Plastic materials. London: Iliffe Books, 1969.
[6] Brandt W, Berko S, Walker WW. Phys Rev 1960;120:1289.
[7] Jean YC. Microchem J 1990;42:72.
[8] Nakanishi H, Jean YC, Smith EG, Sandreczki TC. J Polym Sci B 1989;27:1419.
[9] Stevens JR. In: Fava RA, editor. Methods of experimental physics, 16. New York: Academic Press, 1980:371.

[10] Moggi G, Bonardelli P. J Polym Sci, Polym Phys 1984;22:357.
[11] Murthy NS, Khanna YP, Signorelli AJ. J Polym Sci Engng 1994;36:1254.
[12] Mackenzie IK. Proceedings of the International School of Physics. Enrico Fermi. Amsterdam: North-Holland, 1983:196.
[13] Ramachandra P, Ramani R, Ravichandran TSG, Ramgopal G, Gopal S, Ranganathaiah C, Murthy NS. Polymer 1996;37:3233.
[14] Kirkegaard P, Pederson NJ, Eldrup M. Report of the Riso National Laboratory, Denmark, 1989, M-2740.
[15] Davies WJ, Pethrick RA. Eur Polym J 1994;30:1289.
[16] Goldanskii AV, Onishuk VA, Shantarovich VP. Phys Stat Sol (a) 1987;102:559.
[17] Tao SJ. J Chem Phys 1972;56:5499.
[18] Eldrup M, Lightbody D, Sherwood JN. Chem Phys 1981;63:51.
[19] Nakanishi H, Wang SJ, Jean YC. In: Sharma SC, editor. Positron annihilation in fluids, Singapore: World Scientific, 1988.
[20] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1955;77:3701.
[21] Deng Q, Sundar CS, Jean YC. J Phys Chem 1992;96:492.
[22] Vinogradov GV, Malkin AYa, editors. Rheology of polymers Moscow: Mir, 1980.
[23] Ramachandra P, Ramani R, Ramgopal G, Shariff G, Thimmegowda MC, Sathyanarayana PM, Ranganathaiah C. Polym Int 1999.
[24] Menicik Z. J Polym Sci, Polym Phys 1973;11:1585.
[25] Adams GC, Stein RS. J Polym Sci, Part A-2 1968;6:31.
[26] Geil PH. Polymer single crystals. New York: Interscience, 1963: 366.
[27] Murasheva YeM, Shashkov AS, Galil-Ogly A. Vysokomol Soedin Ser A 1979;21:882.
[28] Eldrup M, Shantarovich VP, Mogensen OE. Chem Phys 1975;11:29.
[29] Djermouni B, Ache H. J Phys Chem 1978;82:2378.
[30] Wikander G. Chem Phys 1982;66:227.
[31] Wikander G, Mogensen OE, Pedersen NJ. Chem Phys 1983;77:159.
[32] Murthy NS, Khanna YP. Signorelli. J Polym Sci Engng 1994;36:1254.