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On the Secondary Relaxation of Substituted Bis-A Polycarbonates

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ABSTRACT: The relaxation behavior of substituted bisphenol-A polycarbonates is investigated in the glassy state by mechanical spectroscopy. Conventional bisphenol-A polycarbonate (BA-PC) is compared with polycarbonates based on 1,1′-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (TMC-PC) and 1,1′-spiro[bis(3,3-dimethyl-6-hydroxyindane)] (SBI-PC) and random copolymers of the latter with bisphenol-A. In SBI-PC the phenyl flip is not just hindered but completely locked due to the chemical bridge via the spiro linkage. Despite the impossibility of phenyl motion, the γ-relaxation is observed for SBI-PC at roughly the same temperature as for the other two polycarbonates. This is real proof that the phenyl motion is not required for the typical γ-relaxation of polycarbonate at low temperature. Consequently, the polymer chain can get its mobility only from the flexibility of the carbonate linkage. It was also found that the width of the γ-relaxation peak in the SBI copolycarbonates decreases systematically with increasing spiro content. This means that in the rather broad peak in BA-PC there is a contribution of a second damping mechanism at the higher temperature side which is affected by the spiro linkage. That damping contribution is therefore ascribed to the phenyl motion. This also explains why the γ-relaxation of polycarbonates with ortho-substituted phenyls occurs at much higher temperatures. There the carbonate motion couples to the phenyl motion due to sterical hindrance, which is not the case in SBI-PC.

Introduction

BA-PC possesses exceptional mechanical properties, especially with respect to the low-temperature impact strength. From the great number of polycarbonates which have been synthesized, the bisphenol-A-based ones turned out to have the best properties.[1] The high impact strength has been related to the low-temperature mechanical loss process which is very pronounced in BA-PC.[2,3] Many studies have been dedicated to the identification of this so-called γ-relaxation.[4] However, no consistent picture has evolved from these studies. NMR techniques identified a strong contribution from phenyl flips around their C1−C4 axis with a small variation of the axis of motion. The carbonate group undergoes only a minor reorientation.[5] Dielectric studies also indicated that the carbonate group does not undergo a major reorientation but rather a small cooperative motion together with the phenyl flip motion.[6] As Jho and Yee[4] pointed out very nicely, there is a major deficiency in the interpretation of NMR and dielectric spectroscopy results with respect to the mechanical significance of the observed relaxations. On the other hand, mechanical measurements do not pinpoint molecular processes but rather measure the bulk response. However, with chemical modification it should become possible to draw conclusions from mechanical measurements concerning the involvement of certain parts of the molecule in a mechanical relaxation process.

In a comparison of an impressive number of substituted polycarbonates, Yee and Smith[2] observed that substitution on the phenyl ring leads to a strong shift of the γ-relaxation to higher temperatures. Symmetrically substituted bisphenols displayed a stronger shift than asymmetrical ones. Substitution on the isopropylidene group, however, did not lead to a significant effect on the γ-relaxation temperature, despite the fact that the glass transition temperature, T_g, was affected substantially. Depending on the stiffness and bulkiness of the substituent, T_g either increased or decreased. On the basis of their extensive experimental base, they arrived at the conclusion that the secondary relaxation is coupled to the phenyl motion but probably involves the whole repeat unit. From the observation that the γ-relaxation can be suppressed by the addition of low M_w diluents (so-called antiplasticizers), a model was given by Fischer et al.[7] that postulates the necessary condition of a minimum free volume fluctuation in order to get the γ-relaxation.

They proposed a local-mode relaxation coupled to the phenyl rotation with no intermolecular cooperativity. Hansen et al.[8] reported a density dependence of the phenylene motion by NMR. On the basis of the same experiment as Fischer et al.,[7] viz. the relaxation behavior of a miscible blend of BAPC and tetramethyl-PC (TM-PC), Jho and Yee came to the conclusion that intermolecular cooperativity exists.[4] By investigating alternating block copolymers of BA-PC and TM-PC of various block lengths, the same authors[4,9] showed that a strong intrachain cooperativity involving between six and nine repeating units, which is comparable to the entanglement molecular weight of the BA-PC melt, occurs. But in a recent molecular dynamics simulation, Shih and Chen[10] concluded that intrachain cooperativity in BA-PC does not involve more than two repeating units.

Apart from the cooperativity, the question of the mechanism of reorientation and relaxation still remains. There is clear evidence for the phenyl motion, but its relevance is not clear yet. It also has been concluded from simulations that the phenyl rotation has a low activation energy. Sung et al.[11] concluded that the rotation is hardly affected by the carbonate group itself. Jones[12] proposed a mechanism of a correlated conformational interchange of two neighboring carbonate groups, e.g. from the trans−trans to the cis−trans state. Such a conformation can then diffuse down a chain. The reorientation of the CO bond is accompanied by a phenyl flip according to Jones. Shih and Chen[10] support that idea of a coupled motion of the carbonate and the

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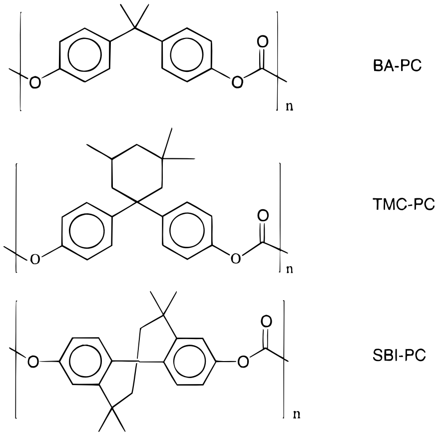

Figure 1. Chemical configuration of the repeating units of BA-PC, TMC-PC, and SBI-PC.

adjacent phenyl rings. In this way only a small activation volume is required, as the bisphenol group between the respective carbonate groups is only slightly reoriented and the chain ends do not translate.

In view of all these observations, it seems interesting to look at the behavior of a special polycarbonate, i.e. the spirobisindane-PC (SBI-PC). The structure of the repeating unit is sketched in Figure 1. The special thing about it is that both the isopropylidene group as well as both phenyl rings are substituted and that due to the spiro coupling the phenyl rotation is completely inhibited. The dynamic mechanical behavior of this PC will be investigated and compared to BA-PC and a new commercially available PC, viz. (trimethylcyclohexyl)-bisphenol-PC (TMC-PC).[13] Its structure is also shown in Figure 1. It has the same molecular weight of saturated substituent (C_9H_{16}) and a T_g comparable to that of SBI-PC, but it is only substituted at the isopropylidene group.

Experimental Section

Materials. The BA-PC used is Makrolon CD 2000/00 from Bayer AG. This is an optical grade without additives like release agents. The molecular weight (M_w) is 20 000 g/mol and the dispersion is about 2.5. The TMC-PC homopolymer was obtained from Bayer AG as a precommercial grade. The molecular weight is slightly higher than that of CD 2000.

SBI-PC and copolymers of various compositions were synthesized in our laboratory as described previously.[14] All samples were compression molded above their glass transition temperature after predrying. Inherent to the molding operation is a thermal quench from above T_g, so the samples were unaged before the mechanical testing.

Mechanical Measurement. Dynamic mechanical analysis was carried out with a DMTA (Mk III of Rheometric Scientific, UK). The samples were loaded in single cantilever bending geometry at 1 Hz. Typical sample cross section was 5 × 0.5 mm and the distance between clamps was 5 mm. The strain amplitude was 64 μm. For the multifrequency tests the frequencies were scanned in steps from 0.3 to 30 Hz while the sample was heated at a rate of 0.5 °C/min. The single frequency measurements at 1 Hz were carried out at heating rates of 2 and 4 °C/min.

Results

As mentioned in the Introduction, the main purpose of this investigation is to look at the low-temperature relaxation behavior of spiro-substituted PC. In Figure 2, the damping, expressed as tan δ, is shown for SBI-PC, BA-PC, and TMC-PC together in the low-temperature regime. As can be seen there, all three polymers have a significant damping peak in the range of interest. The damping maximum of TMC-PC is in between those of BA-PC and SBI-PC. Obviously, the bulky substituent in TMC-PC does not affect the relaxation behavior significantly. This is in agreement with earlier investigations of Yee and Smith[2] indicating that substitution on the isopropylidene does not affect the damping at low temperatures.

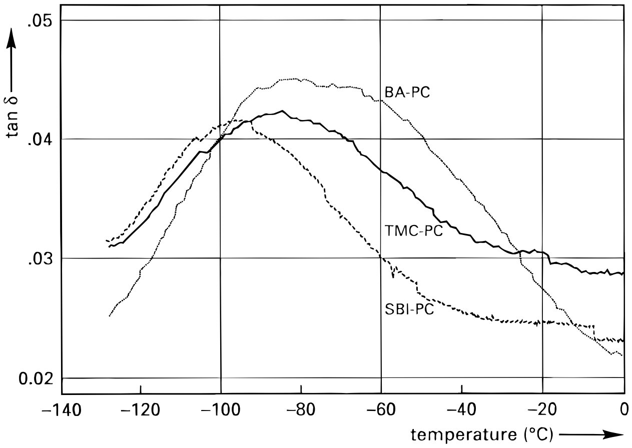

Figure 2. Low-temperature mechanical loss spectra of BA-PC, TMC-PC, and SBI-PC, expressed as tan δ, as obtained from DMTA in the bending mode with a heating rate of 2 K/min.

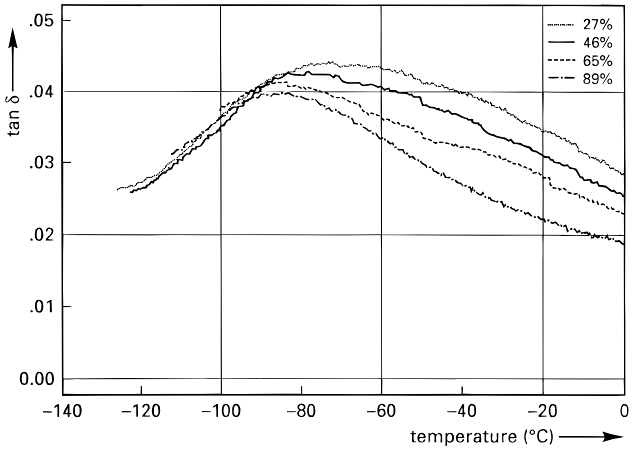

Figure 3. Mechanical loss spectra of copolymers of SBI and BA-PC with the compositions as indicated in vol % SBI.

The most important observation, however, is the fact that SBI-PC also displays a low-temperature damping maximum. The maximum is even shifted to a little lower temperature than that of BA-PC. Their intensities are comparable, but the width of the peak of SBI-PC is significantly smaller. This is unexpected since substitution on the phenyl ring should lead to a suppression of the low-temperature damping peak. The observed slight shift to lower temperature would even suggest that the underlying relaxation mechanism is rather facilitated by the substitution. An explanation for this still needs to be given.

Apart from the mere existence of the γ-relaxation in SBI-PC, it is also interesting to look more carefully at the narrowing of the peak. This decrease of the damping at the high-temperature side of the maximum is demonstrated nicely by comparing random copolymers of SBI- and BA-PC of different compositions. In Figure 3 the tan δ curves are shown for four copolycarbonates with SBI contents of 27, 46, 65, and 89 wt %, respectively. (The higher position of the maxima on the temperature axis compared to Figure 2 is due to a higher heating rate.) This clearly shows that the damping decreases systematically on the right-hand

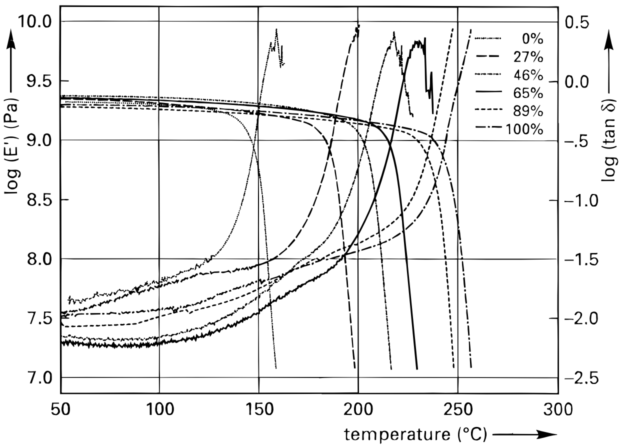

Figure 4. Storage moduli and loss angles of copolymers as in Figure 3 together with CD 2000 (0% SBI) and 100% SBI-PC at elevated temperatures with a heating rate of 4 K/min.

side of the maximum. The maxima shift a little to lower temperatures. The left-hand side of the maximum is barely affected. The effect of addition of SBI repeating units reaches very far into higher temperatures. This means that the process that is suppressed upon addition of SBI comonomer is smeared out over a broad temperature range. The gradual depression with composition indicates that the contributions to the damping are based on a statistical weighing rather than specific long-range intramolecular processes. The latter should already be suppressed at lower concentrations of SBI comonomer.

The damping spectra of the polymers at higher temperatures are displayed in Figure 4. As can be seen, the glass transition is shifted to higher temperatures with increasing spiro content. (The damping above T_g is not well-resolved because the sample were not stiff enough at those temperatures.) It turns out that the shift of T_g is relatively strongest for small SBI content. In a previous study it was shown that the entanglement molecular weight, M_e, a measure for the chain stiffness, also increases with SBI concentration.[14] The damping curves in Figure 4 also show a secondary maximum assigned as β-relaxation in the present context. This part of the spectrum turned out to be very sensitive to the thermal history of the samples, which is typical for β-relaxation. The curves of Figure 4 were obtained during the second scan in the DMTA. In the first scan of the quenched samples the β-relaxation was much more pronounced. Note that the damping below the β-relaxation is very low for the copolymers. There is no secondary relaxation in the temperature range, where the ortho-substituted PC's like tetramethyl or tetrabromo bis-A PC show a pronounced relaxation maximum.[2,3]

Discussion

In Figure 5 the conformation of a trimer of SBI-PC is sketched again for clarity. This conformation is the result of an optimization of the geometry for minimum energy in a MM mode of the Chem-X modeling package.[17] The sketch clearly shows the bulkiness of the SBI bisphenol. The spiro linkage leads to a strain in the indane ring and does not allow any relative movement at all. The dimethyl substitution on the indane enlarges the volume necessary for a rearrangement even further. This makes it very unlikely that the reorientation process would be identical to that proposed for BA-PC. It is clear from the molecular configuration that there is only one part of the molecule which is not directly affected by the substituents; that is the carbonate group. It is interesting to note the significant difference between SBI-PC and the phenyl-substituted PC's reported in literature, namely the fact that the substitution is not on the position ortho but meta to the carbonate substituent. This means that although the phenyl motion is locked in and the whole part between the carbonates is rigid, the carbonate itself is not hindered sterically by the substituents like it is in the case with ortho substitution. In the SBI-PC the carbonate group can move more or less in the same way as in BA-PC. In the ortho-substituted case, both motions get coupled and the relaxation peak obviously shifts to a much higher temperature. From the fact that the major part of the γ-relaxation is retained in the SBI-PC, it can be concluded that the reorientation mechanism must originate from the mobility of the carbonate group. This means that proposed models for the reorientation process that involve the so-called π-flip or a similar coupling of the phenyl groups can be abandoned.[15] In fact it has been pointed out by Sung et al.[11] that the ring flips are neither necessary for the reorientation of the carbonate groups nor essential to the model proposed by Jones[12] (cis–trans isomerization). The dissipative relaxation process is of course not limited to the motion of the carbonate unit. It will involve the complete repeating unit and neighboring chains. The fact that this process appears to be hardly affected by the spiro linkage remains surprising, however.

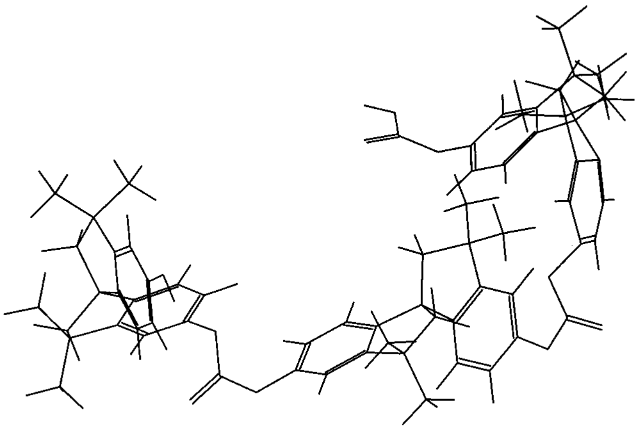

Figure 5. Example of conformation of SBI-PC trimer as obtained with ChemX by minimizing the energy (in MM mode).[17] Cis and trans conformations were chosen arbitrarily.

An explanation for the asymmetric effect in the γ-relaxation of SBI copolymers can be given by assuming that the maximum of BA-PC is composed of two overlapping maxima, as also indicated recently by Lee et al.[16] Within that interpretation, the narrowing of the relaxation peak in the SBI-PC would be a consequence of the suppression of the submaximum at the high-temperature side in BA-PC only. Since the spiro coupling essentially freezes the individual phenyl motion, this damping contribution should be related to the phenyl motion. Molecular dynamic simulations have indicated that both the phenyl and the carbonate rotation will have comparable activation energies.[11] The bulky substituent in TMC-PC should also be quite effective in hindering the phenyl rotation. Indeed, the damping peak of TMC-PC was found in between those of SBI-PC and BA-PC in Figure 2. It would be interesting to do NMR measurements on SBI-PC in order to find out whether the observed π-flip in BA-PC indeed is due to a second relaxation mechanism or is merely an indication of an overall mobility. In the latter case, the phenyl motion should also be present in the SBI-

PC. Otherwise this would confirm the presence of two distinct mechanisms in BA-PC.

The point still open is the question why the γ-relaxation maximum shifts to lower temperature with increasing SBI content. The fixation of the phenyl rings should enlarge the barrier for the motion of the carbonate unit since the adjacent phenyl rings cannot give way to it. Consequently, the maximum could be expected to occur at higher temperatures. A reasonable explanation can come from the reduced packing density of the SBI-PC compared to BA-PC. The density of SBI-PC at room temperature is only 1.11 g/cm^3, compared to 1.19 g/cm^3 for CD 2000. This can lead to a higher local free volume for the carbonate motion, thus facilitating the reorientation by reducing the intermolecular coupling. This is consistent with the observed gradual downward shift of the peak temperature in the SBI copolycarbonates.

In the remaining discussion a different point will be addressed. Since for the SBI copolycarbonates both the secondary relaxation as well as the rheological properties in the melt state were investigated,[14] this gives us the opportunity to test an empirical correlation proposed by Wu[18] between the secondary relaxation maximum and the chain stiffness expressed as characteristic ratio C_∞:

$$\frac{T_\beta}{T_\alpha} = 0.135 + 0.082C_\infty \tag{1}$$

where α denotes the glass transition and β the secondary transition, which is the γ-relaxation in the present context. This affine linear correlation means that the proximity of the secondary transition to the glass transition is a measure for the chain stiffness; the stiffer the chain, the closer the relaxation processes. In the SBI copolycarbonates, C_∞ increases,[14] the secondary transition maximum decreases slightly, and the T_g increases. This means that within the series of copolycarbonates we observe a correlation opposite to that reported by Wu. The correlation is also nonlinear and weaker than that of Wu. In order to comply with the correlation proposed by Wu, SBI-PC should have a γ-relaxation at room temperature. This means two things; namely, that the correlation given by Wu is not valid in general and that SBI-PC obviously represents a special case of polymer with a high chain stiffness and high T_g combined with a low-temperature secondary transition. It is therefore an interesting candidate to test concepts for the brittleness of polymers. The high ductility of BA-PC is usually ascribed to the prominent γ-relaxation peak at low temperature. On the other hand, it was shown that the brittle failure of polymers is related to the entanglement density of polymers.[19,20] As long as the correlation of Wu is valid, a secondary relaxation at increased temperature also means a lower entanglement density so one cannot discriminate between the two effects. SBI-PC, however, allows such a discrimination since it has both a prominent loss-peak at low temperature and a low entanglement density. Therefore it will be interesting to investigate the impact behavior of SBI-PC.

Conclusions

BA-PC and the modified polycarbonates, viz. TMC-PC, SBI-PC, and copolymers of the latter with bisphenol-A, display a γ-relaxation at similar temperatures. Compared to BA-PC, the maximum position of the loss peak is shifted a little to lower temperatures and its width is reduced for all investigated polymers.

From this we can conclude that the γ-relaxation peak of BA-PC originates from the motion of the carbonate group, since the phenyl is totally rigid in the spiro-linked bisphenol of SBI-PC. Models that take the phenyl motion as an essential mechanism of the γ-relaxation can be abandoned.

From the fact that the γ-relaxation peak decreases systematically on the high-temperature side with increasing spiro content in the SBI copolycarbonates, we conclude that the phenyl motion contributes as a separate mechanism to the damping on that part of the γ-relaxation peak of BA-PC.

The dramatic shift of the γ-relaxation peak to higher temperatures which is described in literature for phenyl-substituted polycarbonates is explained by a coupling of the carbonate and the phenyl motion in all these cases, where the phenyl rings are substituted in the ortho position to the carbonate. In SBI-PC the phenyl motion is prohibited, but the carbonate motion is not sterically hindered.

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