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Branching Reactions in Polycarbonate: A Density Functional Study

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ABSTRACT: Branching can have a dramatic effect on the properties of polymers, and bisphenol A polycarbonate (BPA−PC) is no exception. We describe here the results of a density functional (DF) study of branching that can occur during transesterification reactions in BPA−PC in the presence of catalysts. We find that sodium phenoxide (NaOPh) can lead to different branched products, because the Na ion can bond to different O atoms simultaneously. Tetraphenylphosphonium phenoxide, which can be used as an alternative catalyst to NaOPh in BPA−PC synthesis, does not lead to branching, because steric hindrance prevents its active sites from approaching the O atoms.

I. Introduction

Polymers formed by the stepwise addition of difunctional units have a one-dimensional topology, examples being polyethylene (PE), polystyrene (PS), and poly(vinyl chloride) (PVC). The topology changes induced by the presence of multifunctional units can result in systems such as branched chains, stars, and cross-linked networks with dramatically different glass and melting transition temperatures, morphologies, size distributions, viscosities, and other properties.[1] Branching may also result in new phases such as gels and rubbers, where the entire system may be viewed as a single cross-linked molecule.[2]

Polycarbonates (PC) are thermoplastic materials with excellent transparency and high impact resistance, and their many applications include optical instruments, electronic appliances, and automobile parts. They can be prepared by the reaction of an aromatic dihydroxy compound [e.g., bisphenol A (BPA)] with a carbonate precursor such as phosgene (interfacial polycondensation) or in a melt by transesterification of BPA with diphenyl carbonate (DPC) (melt method, MM). The latter avoids the use of phosgene and chlorinated solvents and has environmental advantages, but branching, cross-linking, and other side reactions caused by temperatures of 200−300 °C can lead to discolored or degraded products. The carboxylic branching structure observed in reactive pyrolysis in MM-PC production[3] indicated that the PC chain is most susceptible to branching at the carbonate group, where transesterification occurs in PC synthesis.[4−6]

In some cases branching is desired, because long-chain branched PC modifications show special shear viscosity behavior that makes them suitable for blow molding applications. The degree of branching can be controlled by branching agents such as THPE [1,1,1-tris(*p*-hydroxyphenol)ethane][7] and polyphenols.[8−10] Krabbenhoft and Boden,[9] for example, reported the production of branched polycarbonates with high shear sensitivity using the ring-opening polymerization (ROP) of cyclic oligomers of BPA carbonates with tri- and tetraphenol reagents.

In recent years, our group has performed numerous theoretical studies of ROP reactions in the BPA−PC melt, including density functional (DF) calculations on the role of different catalysts and additives in PC synthesis.[5,6,11] We have also developed a simplified model of ROP in BPA−PC melts[12] that has been extended to include a varying number of active (catalytic) sites,[13] and multifunctional units.[14] The multifunctional units lead to branching and, under certain conditions, to gel formation. This work is extended here to a DF study of a two-step branching reaction in BPA−PC. The first stage involves the reaction between phenyl 5-*tert*-butyl-2 sodiumoxybenzoate (PBNaOB) and DPC (Figure 1b). The former is a branching initiator in a polycarbonate melt formed from DPC+ (one-sided-*tert*-butyl terminated DPC) by a Fries rearrangement reaction catalyzed by sodium phenoxide (NaOPh). The most stable form of PBNaOB (Figure 1a) underscores the ability of Na to form "hypervalent" bonds with more than one O atom. The products of this first step are NaOPh (Figure 1d) and the "branched" carbonate (Figure 1c), and the second stage examines how the reaction of these two molecules can lead to a different branched product. The labeling of the atoms is shown in Scheme 1.
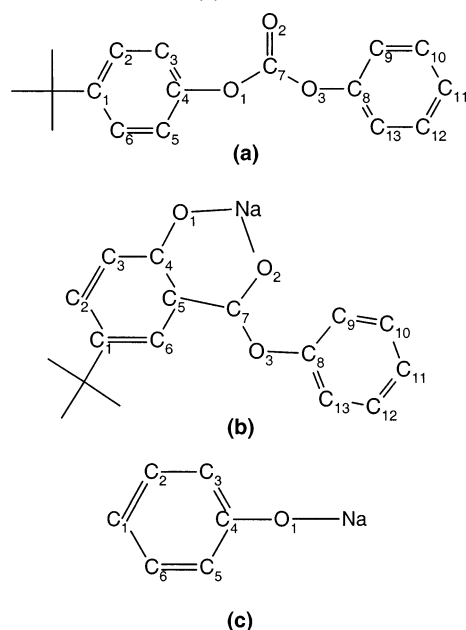
We focus on the transesterification pathway[3] and the role of the catalyst NaOPh. We find that the Na can interact with several oxygen atoms simultaneously, and branching is enhanced by the proximity of the active sites for transesterification. In practice, the choice of catalyst and melt temperature is crucial for the implementation of the melt method,[4,15,16] and we compare NaOPh with tetraphenylphosphonium phenoxide (PPh$_4$-OPh), for which steric hindrance prevents branching. Our earlier studies have shown that both NaOPh (and LiOPh) activate the ROP of BPA−PC,[5] and NaOPh and PPh$_4$OPh catalyze chain growth in PC.[6] Their industrial use is well documented.[17−20]

In section II, we give necessary details of the calculations, and in section III, we present the results for a sequence of reactions involving NaOPh and calculations for PPh$_4$OPh. Our concluding remarks are given in section IV.

II. Method of Calculation

The method of calculation has been described in detail previously.[21] The electron−ion interaction is represented by ionic pseudopotentials with the (nonlocal) form suggested by Troullier and Martins.[22] We use periodic boundary conditions and an orthorhombic unit cell with

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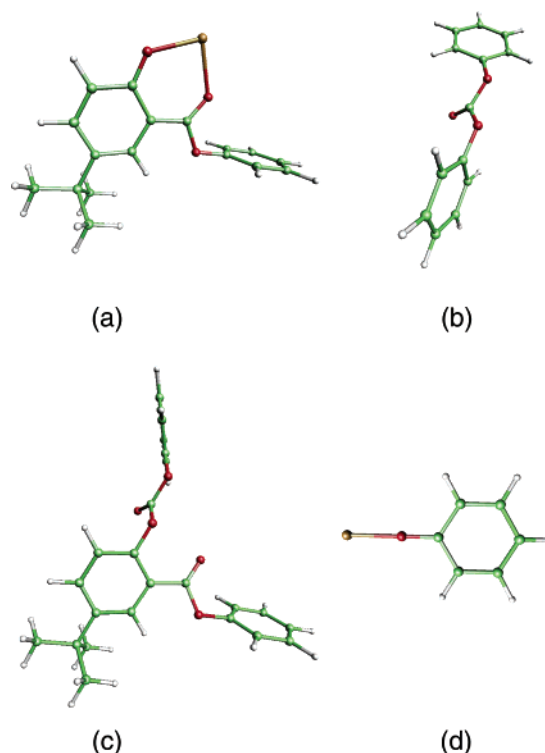* Corresponding author. E-mail: r.jones@fz-juelich.de.

(a)

(b)

(c)

(a) (b)

(c) (d)

Figure 1. Structures of (a) PBNaOB, (b) DPC, (c) branched PC ortho ester, and (d) sodium phenoxide. Key: C, green; O, red; H, white; Na, brown.

lattice constants chosen to ensure that the images of the reacting systems are well-separated. The orbitals are expanded in terms of a plane wave basis (kinetic energy cutoff of 35 au) using a single point ($\mathbf{k} = 0$) in the Brillouin zone. This basis has been shown to provide a reliable description of energy differences in these systems, and we use the approximation of Perdew, Burke, and Ernzerhof (PBE)[23] for the exchange-correlation energy. Vibration frequencies are calculated using linear response theory.

As in our earlier simulations, we have studied the energy surfaces by varying a reaction coordinate R_C, such as the distance between the C atom of a carbonate group and an O atom on a phenoxyl group, until a structural transformation or a large energy change takes place. For large values of R_C (typically >5 Å), the weak interaction between the reactants allows changes of 1 Å, but progressively shorter steps (0.5−0.1 Å) become necessary as the reaction proceeds. For each value of R_C, we relax *all* other degrees of freedom of the structure using molecular dynamics,[24] until the energy gradients along the unconstrained directions are less than an appropriate tolerance. A single reaction coordinate is not sufficient to describe most reactions, and others are adopted as necessary. There is no guarantee, of course, that this—or any other—method can determine the optimum reaction path, but the present calculations have been very extensive. Structures corresponding to minima in the energy surface are generally relaxed, i.e., the constraint on R_C is removed.

III. Branching Reactions of Polycarbonate

A. Structures and Properties of Reactants. The reactants are shown in Figure 1, and the structural parameters, effective charges (ESP charges calculated from a fit to the electrostatic potential), dipole moments, and characteristic vibration frequencies are given in Table 1. In both NaOPh and PBNaOB an unsaturated oxygen atom (O_1) interacts with Na, and PBNaOB has an additional Na−O interaction of comparable strength with the carbonyl oxygen (O_2) (see Table 1). The large dipole moment results from the charge transfer from

Na to the oxygen and other atoms, and the increased Na−O coordination makes the individual Na−O contacts weaker than in NaOPh. The dihedral angles around the ester group differ markedly from those in DPC+ due to the C−C ester linkage. PBNaOB has a mirror plane with the peripheral phenyl group rotated by 90° from the plane of the other phenyl group.

The calculated vibrational densities of states of DPC+ and PBNaOB are similar, but the presence of Na and the related charge transfer (see Table 1) causes a red shift of over 100 cm^{-1} in the C−O double bond stretch. A strong peak near 360 cm^{-1} in PBNaOB is absent for DPC+, and analysis of the vibrational eigenvectors shows that this mode involves bending of the O−Na−O contact coupled with "breathing" of the phenoxyl and ester groups. The small blue shift in the lowest two of the three C−H stretching peaks is related to Na-induced charge transfer from the terminal butyl-group in PB-NaOB.

B. Reactions involving NaOPh. Transesterification caused by the nucleophilic attack of PBNaOB on DPC is similar to the reaction observed in PC synthesis between a chain-terminating phenoxide group (NaOPh···) and DPC. The initial reaction coordinate (R in Table 2) is the distance between the carbonate carbon in DPC and the phenoxyl oxygen (O_1) in PBNaOB. The structural changes during the reactions are shown in Figures 2 and 3, and the corresponding changes in total energy for all reaction coordinates (R, S, T, D, U, see below) are shown in Figure 4 and Table 2.

The starting configuration consists of PBNaOB and DPC molecules at $R = 8.0$ Å, where the interaction between molecules is negligible and the energy is defined to be zero. Changes in R, initially 1 Å, were reduced as the reaction proceeded. The total energy of the system decreases at first due to the attraction between the Na cation and carbonyl oxygen, leading to

Table 1. Results of DF Calculations for Molecules in Figure 1: Bond Lengths in angstroms, Bond and Dihedral Angles in degrees, Atomic Charges (e), Dipole Moments (debye) and Vibration Frequencies (cm^{-1})[a]

atoms	DPC+	PBNaOB	NaOPh
C_7-O_1	1.36	(3.01)	
C_7-O_2	1.21	1.24	
C_7-O_3	1.37	1.41	
C_4-O_1	1.41	1.29	1.32
C_8-O_3	1.41	1.40	
C_7-C_5	(2.98,[b] 3.56)	1.45	
$Na-O_1$		2.24	2.11
$Na-O_2$		2.35	
$O_1-C_7-O_2$	128.0		
$O_1-C_7-O_3$	104.7		
$O_2-C_7-O_3$	127.3	117.4	
$C_4-O_1-C_7$	120.1		
$C_7-O_3-C_8$	118.3	116.1	
$C_5-C_7-O_2$		129.9	
$C_5-C_7-O_3$		112.8	
C_4-O_1-Na		132.9	180.0
C_7-O_2-Na		128.5	
O_1-Na-O_2		80.1	
$C_3-C_4-O_1-C_7$	40.2		
$C_4-O_1-C_7-O_2$	10.2		
$O_2-C_7-O_3-C_8$	4.3	0.0	
$C_7-O_3-C_8-C_9$	56.5	90.0	
$C_4-C_5-C_7-O_2$		0.0	
$Q(C_7)$	0.88	0.95	
$Q(O_1)$	−0.41	−0.87	−1.15
$Q(O_2)$	−0.55	−0.75	
$Q(O_3)$	−0.43	−0.53	
$Q(C_4)$	0.38	0.72	0.84
$Q(C_5)$	−0.25	−0.64	−0.38
$Q(C_8)$	0.37	0.53	
$Q(Na)$		0.89	0.93
dipole	0.7	7.9	12.1
C_7-O_2 stretch	1760	1660	
$C_7-O_{1,3}$ stretch	1130−1160	1130	
C_8-O_3 stretch	1160−1210[c]	1190	
C_7-C_5 stretch		1310	
C_4-O_1 stretch		1480	1480
Na−O stretch		490−510	570

[a] The values in parentheses do not involve chemical bonding.
[b] For symmetry reasons, we give the C_7-C_3 distance. [c] Includes also C_4-O_1 stretching.

a minimum of −13.4 kcal/mol at 3.5 Å for a structure where Na has bonds between 2.3 and 2.5 Å with three O atoms (O_1,O_2 and O_c, the carbonyl O of DPC). Constraint-free optimization leads to an energy of −14.6 kcal/mol for $R = 3.80$ Å (see Table 1), which is a measure of the strength of the pairwise interaction between Na and O_c. Further reduction of R leads to steric hindrance and a rapid increase in energy. For $R < 2.0$, the total energy of the system is positive, and the DPC carbonate group distorts from its planar sp^2 configuration. The phenoxyl O (O_1) gradually loses its Na contact, and the single bond formed with the carbonate C leads to a tetrahedral sp^3 configuration at $R = 1.5$ Å.

Reduction of R to 1.3 Å does not favor the reaction, because interactions with O_1 and O_2 restrict the motion of Na and prohibit the formation of new Na−O bonds. We have stretched one of the carbonate C−O single bonds and applied constraints to the Na−O distance and dihedral angles involving Na. Only the first of these (S in Table 1) led to a small increase in the total energy to a maximum (at a C−O separation of 1.9 Å) of 7.98 kcal/mol, over 20 kcal/mol higher than the previous minimum. We expect (see below) that this maximum could

be made smoother by combining the stretch S with a displacement of Na. Increasing the C−O separation leads to a planar (sp^2) carbonate group, while Na retains its two oxygen contacts. The phenoxyl radical formed moves until Na is above the phenoxyl ring, and the energy has a local minimum (+2.79 kcal/mol) for $S = 2.6$ Å (relaxation yields +2.53 kcal/mol for $S = 2.74$ Å; see Table 2).

The interaction between the phenoxyl radical and Na is increased when the former is removed from the branched product by applying the same constraint (S). This leads to a minimum in the total energy (−1.69 kcal/mol for $S = 3.97$ Å) when the system is relaxed (from 3.2 Å) without constraints. The result is a branched molecule with three aromatic groups linked to carbonate and ester groups, together with NaOPh where Na forms three Na−O bonds (with lengths 2.29, 2.54, and 2.65 Å) and one low-energy hydrogen bond between phenoxyl oxygen O_p and an aromatic H. The difference of over 10 kcal/mol between the energy minima arises both from steric hindrance (O−O repulsion, dihedral angles) and the weakened Na−O bonds.

The branched PC ester with three phenyl groups (Figure 1c) is obtained by performing separate calculations on the products of the previous reaction, PC ester and NaOPh. The absence of the oxygen-binding Na during optimization means that O−O repulsion moves the carbonyl O's of the carbonate and ester groups apart, leading to a tilt of the carbonate group and changes in the orientation of the peripheral phenyl group. The energy difference between the reactants and end products (separated "PC ortho ester" and NaOPh) is 25.2 kcal/mol. The product molecules have one fewer Na−O bond (over 10 kcal/mol), and the repulsion between the carbonyl O's of the ester and carbonate groups changes some dihedral angles. The energy difference is even larger if Na remains bound to the "PC ortho ester", with formation of a radical or ionic phenoxyl. This differs from our earlier ring-opening polymerization study,[5] where the number and nature of the bonds in reactants and product were identical and there was a small energy difference.

The vibrational density of states of the PC ortho ester are very similar to those of DPC+. There is a splitting of ester and carbonate C−O double bond stretching around 1750−1800 cm^{-1}, and a blue shift of C−H stretch modes is related to the charge removal from the butyl group (the molecule has a dipole moment of 4.6 D). The "breathing" of the ester and nearby aryl groups is reduced to 300 cm^{-1} without Na.

The stability of the ester group against transesterification at the defect site of a PC chain has been studied by reducing the separation between an NaOPh molecule and the ester group of the branched PC ester. These molecules are the products of the previous reaction, and the simulation was started from the corresponding local energy minimum. The new reaction coordinate (T; see Table 2 and Figure 4) is the distance between the O_p and ester C. The starting configuration corresponded to $T = 4.25$ Å, and initial changes in T were 0.5 Å.

Reducing the separation of the molecules leads to a slower rise in total energy than in the first reaction, indicating greater flexibility in the system. At 2.4 Å (+1.19 kcal/mol), the energy rises more rapidly, and the increased interaction between the O_p and ester C causes the ester group to distort from planarity (sp^2). The reduction of T to 1.6 Å (+10.2 kcal/mol) leads to a

Table 2. Branching Reaction Energetics of BPA−PC: Reaction Coordinates (Å, for Labels See Text) and Total Energies (kcal/mol)

step	reaction coordinate	energy	step	reaction coordinate	energy
1	$R = 8.0$	0.00	18	relaxed ($T = 4.25$)	−1.69
2	$R = 7.0$	−0.39	19	$T = 3.75$	−1.25
3	$R = 6.0$	−1.26	20	$T = 3.25$	−0.60
4	$R = 5.0$	−3.77	21	$T = 2.75$	+0.22
5	$R = 4.0$	−11.2	22	$T = 2.4$	+1.19
6	$R = 3.5$ (3.80^a)	−13.4 ($−14.6^a$)	23	$T = 2.1$	+4.00
7	$R = 3.0$	−12.4	24	$T = 1.8$	+7.96
8	$R = 2.5$	−8.11	25	$T = 1.6$	+10.2
9	$R = 2.2$	−3.83	26	$T = 1.6$ and $D_1{}^b$	+12.7
10	$R = 1.9$	+2.47	27	$T = 1.6$ and $D_2{}^b$	+16.0
11	$R = 1.6$	+3.75	28	$T = 1.5$ and $D_2{}^b$	+17.0
12	$R = 1.5$	+4.45	29	$U = 1.8$	+16.6
13	$R = 1.5$ and $S = 1.7$	+5.30	30	$U = 2.1$	+15.6
14	$S = 1.9$	+7.98	31	$U = 2.5$	+11.9
15	$S = 2.2$	+4.47	32	$U = 3.0$ ($U = 3.50^a$)	+9.00 (8.07^a)
16	$S = 2.6$ (2.74^a)	+2.79 ($+2.53^a$)	33	$U = 3.5$	+9.82
17	$S = 3.2$	−0.54	34	$U = 4.0$	+10.3
18	relaxed ($S = 3.97^a$)	$−1.69^a$	35	$U = 4.5$	+9.66
			36	relaxed ($U = 4.17^a$)	$+9.09^a$

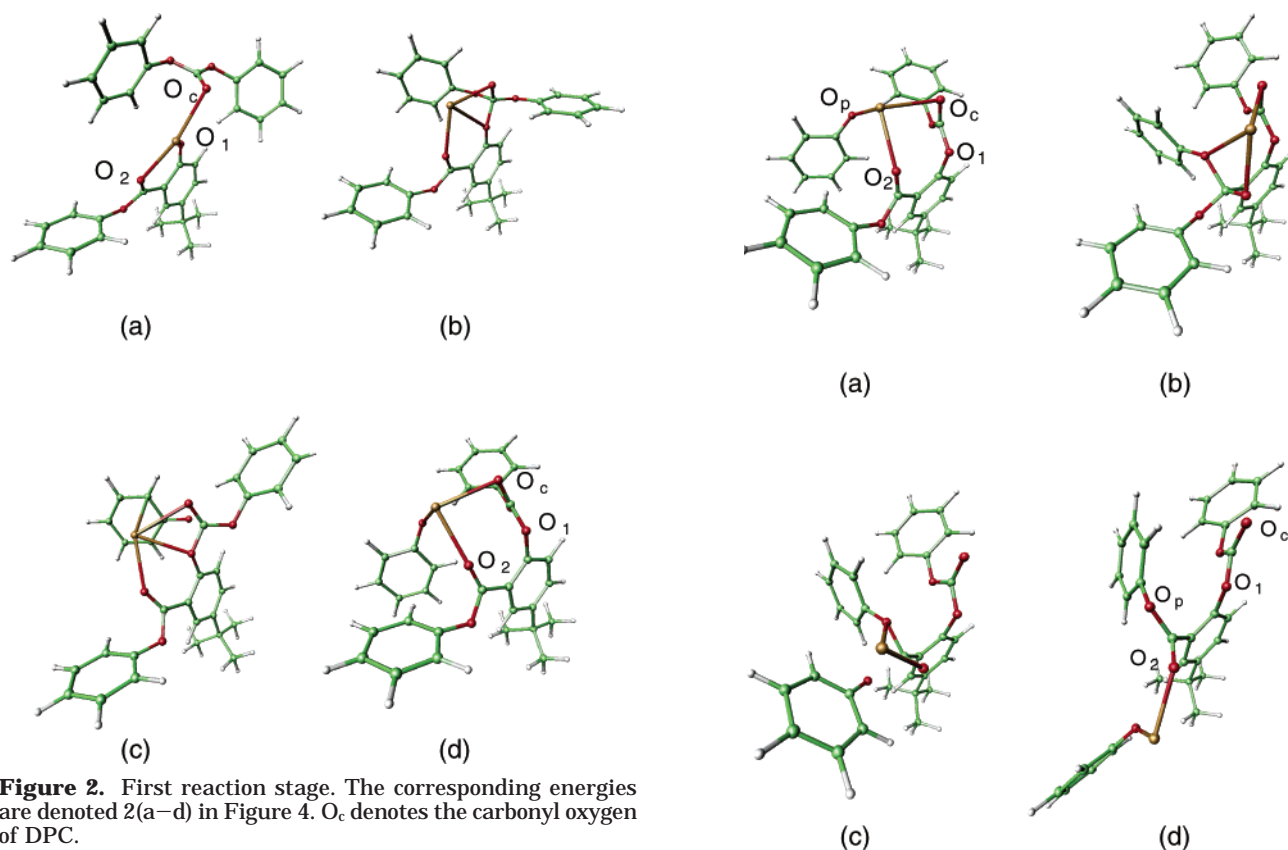^{a} Local minimum obtained by removing the most recent contraint. ^{b} Dihedral angle changes are 25° each.

Figure 2. First reaction stage. The corresponding energies are denoted 2(a−d) in Figure 4. O_c denotes the carbonyl oxygen of DPC.

Figure 3. Second reaction stage. The corresponding energies are denoted 3(a−d) in Figure 4. O_c denotes the carbonyl oxygen of DPC, and O_p is the phenoxyl oxygen.

tetrahedral (sp³) configuration, in analogy to the carbonate group in the previous reaction.

The energy increase of 12 kcal/mol over the starting configuration arises from changes in Na−O bonds (especially in the initial Na−O bond of NaOPh) and the energy barrier between the sp² and sp³ configurations of the ester group. Changing the length of the C−O bond connecting the ester group with the peripheral phenyl group does not cause it to break, since the Na−O interaction prevents the Na from approaching this C−O bond. We have chosen a dihedral angle constraint (involving Na and atoms from the ester group, denoted by D_1 in Table 2 and Figure 4) together with the reaction coordinate T. The second displacement of Na (D_2) results

in an abrupt breaking of one of the initial Na−O contacts and an increase in energy to 16.0 kcal/mol.

Changing T and the Na displacement (dihedral constraint) in the ester group weakens the C−O bond, which is 1.645 Å long for the energy maximum +17.0 kcal/mol at $T = 1.5$ Å. Neither additional displacements of Na nor reduction of T broke this bond. Following our experience in reaction 1, we adopted the reaction coordinate U (see Table 2), which increases the length of the C−O bond. We find that small displacements of U (up to 1.8 Å) lower the total energy and break the
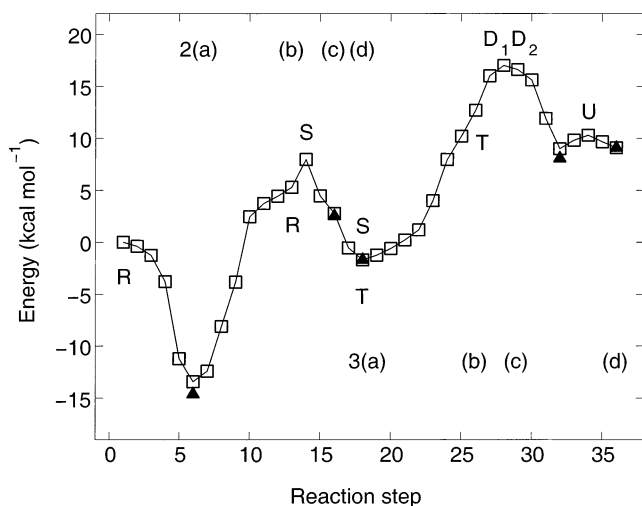
Figure 4. Change in total energy during reactions (see Table 2). Squares show the energies for the reaction coordinates R, S, T, D, and U; solid triangles show the corresponding values without constraints. The correspondence to the structures in Figures 2a–d and 3a–d is also shown.

C–O bond. The phenoxyl O moves away from the ester group, which gradually adopts a planar configuration, and the ring of the phenoxyl radical moves closer to Na. This leads to a stable minimum (+9.00 kcal/mol at 3.0 Å), which relaxes to +8.07 kcal/mol at 3.50 Å). Here Na has one O contact and interactions with the phenoxyl ring, and the substituted phenoxyl O has two low energy hydrogen bonds with aliphatic and aromatic hydrogens of the branched PC ester.

The system goes over a small energy barrier on further increasing U, and the relaxed structure (energy +9.09 kcal/mol at $U = 4.17$ Å) corresponds to NaOPh interacting with the branched PC ortho ester. The energy is 11 kcal/mol higher than in the starting configuration, reflecting the presence of two (i.e., one less) Na–O bonds. There is also a contribution from the weak hydrogen bond between NaOPh and the PC ortho ester.

C. Reactions involving PPh₄OPh. The Na-catalyzed PC synthesis induces unfavorable branching side reactions related to the ability of Na to bind several oxygens simultaneously, so that the active sites are close to each other. We now discuss the possibility of hindering branching reactions by using the tetraphenylphosphonium (PPh₄⁺) cation. The ionic radius is much larger than in Na⁺, and four phenyl groups increase the possibility of steric hindrance. An earlier study[6] showed that the complex of PPh₄ with a phenoxyl ion catalyzes exchange reactions in a manner very similar to NaOPh, although the energy barriers are higher.

A parallel study to the reaction with NaOPh would be excessively demanding of computer resources in the case of PPh₄OPh, but we have performed calculations that shed light on the differences between PPh₄OPh and NaOPh. First, we have placed the PPh₄⁺ cation above the branching initiator (PBNaOB without Na⁺, Figure 5b) and optimized the geometry. We have then moved the constituents artificially close to each other (P–O distance 2.2 Å) and optimized the resulting structure (Figure 5a). The properties of these two structures and those of PPh₄⁺ and PPh₄OPh are given in Table 3.

The isomers in Figure 5 differ, in particular, in their P–O separations (Figure 5a, 2.64 Å; Figure 5b, 3.50 Å). The isomer shown in Figure 5b has more low-energy hydrogen bonds between the aromatic H atoms of PPh₄
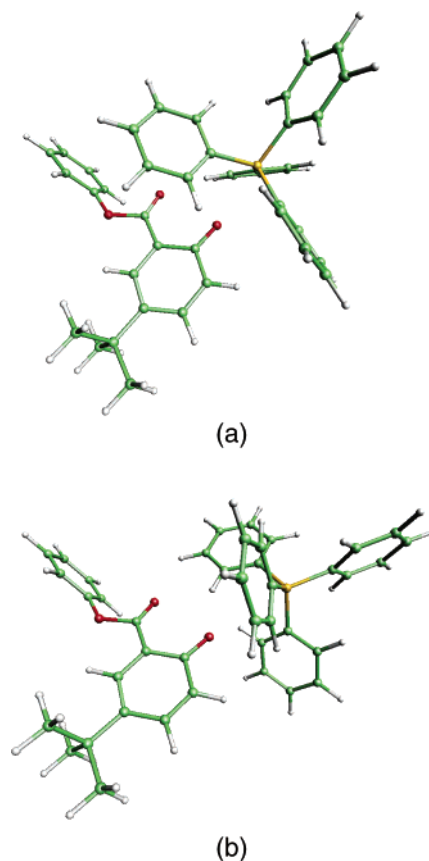

(a)

(b)

Figure 5. Structures produced by the reaction of PPh₄⁺ with PBNaOB without Na⁺ (Figure 1c). Key: C, green; O, red; H, white; P, yellow.

and the O atoms, and it is 1.71 kcal/mol more stable than that in Figure 5a. The ESP charges ($0.7e$ in PPh₄ in both cases) and the large dipole moment imply a significant electrostatic component in the intermolecular interaction, particularly in Figure 5b. There is one (weak) P–O chemical bond and steric hindrance of the other, a qualitatively different picture from PBNaOB. These calculations indicate that the PPh₄⁺ ion cannot approach the branching initiator and will be much less effective than Na⁺ in bringing together the active sites of PC chains that lead to branching.

IV. Discussion and Concluding Remarks

Branching of chains in a polymer can lead to large changes in its properties, sometimes beneficial, sometimes less so. The process often involves complicated, multistep reactions whose details can only be inferred from the nature of the product and experience with other reactions. We have studied here a two-step reaction in BPA–PC that provides a possible branching mechanism following the Fries rearrangement of a carbonate group during the melt process of PC manufacture. We focus on the transesterification process and on the role of the catalyst, sodium phenoxide (NaOPh). We have studied the energy surfaces using density functional calculations with a gradient-corrected (PBE) approximation to the exchange-correlation energy and a pseudopotential description of the electron–ion interaction.

The calculations show that the Na ion in NaOPh can interact simultaneously with several oxygen atoms, providing both a mechanism for branching and a variety of possible products. Calculations for tetraphenylphosphonium phenoxide (PPh₄OPh) indicate that the active

Table 3. Properties of Two PPh$_4^+$ Analogs of PBNaOB Compared to Tetraphenylphosphonium Phenoxide (PPh$_4$OPh) and Tetraphenylphosphonium Cation (PPh$_4^+$)^a

atoms	Figure 5a	Figure 5b	PPh$_4$OPh^b	PPh$_4^+$
P$-$O$_{1d}$	2.84	3.50	2.58	
P$-$O$_{2d}$	4.45	5.31		
O$_{1d}-$H$_{1i}$	2.36	2.03		
O$_{2d}-$H$_{1i}$	2.09	2.43		
O$_{1d}-$H$_{2i}$		2.47		
O$_{2d}-$H$_{3i}$		2.48		
P$-$C$_i$	1.81, 1.85	1.81, 1.82	1.86, 1.90	1.81
P$-$O$_{1d}-$C$_d$	138.9	157.8		
C$_i-$P$-$O$_{1d}{}^c$	176.2	166.8	170.5	
C$_i-$P$-$C$_i$	103.2$-$114.5	106.0$-$112.5	99.6$-$123.9	107.5$-$110.6
Q(P)	-0.08	-0.33	-0.33	-0.21
Q(C$_i$)	0.06, 0.22$-$0.40	0.22$-$0.34	0.16, 0.32$-$0.48	0.20, 0.30
Q(O$_{1d}$)	-0.60	-0.48	-0.62	
Q(O$_{2d}$)	-0.52	-0.49		
Q(PPh$_4$)	0.69	0.70		1.0
dipole	9.9	14.8	8.5	0.2

^{a} Subscripts d and i refer to the branching initiator and PPh$_4^+$, respectively. Bond distances are in angstroms, and bond angles are in degrees. ^{b} From ref 6. ^{c} With respect to the peripheral phenyl group.

site is prevented from approaching the O atoms, and branching reactions should not take place. We expect that lithium phenoxide should show similar behavior to NaOPh, in line with our experience with the reactions of both with the cyclic tetramer of BPA$-$PC. The Li ion is somewhat smaller than Na, and there are differences in detail, but the energy barrier and overall picture are similar.[5]

Earlier work in this series has shown that DF calculations can provide insight into the course of complex reactions involving many atoms. Applications have included ring-opening polymerization of BPA$-$PC cyclic oligomers, exchange reactions involving diphenyl carbonate with NaOPh and PPh$_4$OPh, and the role of epoxide and phosphite additives in BPA$-$PC. The present work provides further evidence of the value of such calculations. These calculations are free of adjustable parameters, but we emphasize that they are extremely demanding of computing resources, both in CPU time and in memory. Nevertheless, we are confident that improvements in numerical algorithms and computer hardware will allow future applications in a wide range of contexts.

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