Quantum-Chemical Study of Structure and Activity of Chain Ends in Metal-Free Anionic Polymerization of Methacrylates

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ABSTRACT: Kinetic and NMR studies of the anionic polymerization of methyl methacrylate using tetraphenylphosphonium and other phosphorus-containing, metal-free counterions indicated an equilibrium between an active ion pair and a corresponding ylide as a dormant species. We present density functional theory (DFT) calculations of the energy difference between the ion pair and the ylide for the ester enolate of methyl isobutyrate with various counterions which support this view. It is possible to establish a correlation based on the calculated energy difference between the ylide and the ion pair and the apparent activity of the chain end. The ylide formed after the first polymerization step is extremely stable compared to the ion pair, whereas after addition of one molecule of methyl methacrylate, the ylide of the dimer is destabilized through steric interactions and the polymerization can proceed much faster. This explains the observation of a pronounced induction period when using the ester enolate of methyl isobutyrate as an initiator.

Introduction

In recent years, considerable efforts have been made to polymerize alkyl (meth)acrylates at a relatively high-temperature keeping all advantages of a living polymerization. The basic problem associated with alkyl (meth)acrylates is the presence of the polar ester group that plays a significant role in propagation and also in side reactions during the polymerization. Ion pairs formed between enolate-like living chain ends and metal counterions tend to aggregate, slow equilibria between aggregated and nonaggregated ion pairs causing broad molecular weight distributions (MWD).[1,2] Moreover, intramolecular solvation of metal counterions by carbonyl groups of penultimate chain units promotes chain termination by an intramolecular Claisen condensation (the so-called “backbiting” reaction).[3,4]

One approach to overcome these problems is to use metal-free counterions, an idea first suggested by Reetz[5] and followed by Sivaram et al.[6] and Fieberg et al.[7] These authors used initiating systems consisting of anions of low nucleophilicity (thiolates, malonates, carbazolides, etc.) with tetrabutylammonium (TBA^+) counterions. However, these attempts have not been very successful, the main drawbacks being considerable induction periods, low initiating efficiencies, and rather broad MWD.[6,7] For TBA^+ salts of various C−H acids as initiators of methyl methacrylate, the presence of chain termination by Hofmann elimination[7] and the equilibrium character of initiation[8] were demonstrated.

Zagala and Hogen-Esch[9a] reported the synthesis of PMMA with a narrow MWD initiated by tetraphenylphosphonium (TPP^+) triphenylmethanide in THF at ambient temperature. Kinetic investigations[10a] led to polymerization rate constants which are 2 orders of magnitude smaller than expected for such large counterions. NMR studies[10b] showed that the TPP^+ ion pairs are in a dynamic equilibrium with dormant ylide species (Scheme 1). When the ester enolate of methyl isobutyrate was used as an initiator with the same counterion, distinct induction periods were observed which was not the case for the triphenylmethanide anions.[10a]

Later it was shown that the structure of the phosphorus-containing cation has a tremendous effect on the apparent reactivity of the chain end. Thus, (1-naphthyl)-triphenylphosphonium (NPP^+) counterions lead to an extremely slow polymerization (half-lives of hours in boiling THF),[9b,c] whereas the bis(triphenylphosphoranylidene)ammonium (PNP^+) gives faster polymerizations than TPP^+.[10c] This was explained by the higher stability of the NPP ylide and the lower one of the PNP ylide, as compared to the TPP ylide. The fastest polymerizations were observed with the P_5^+ phosphazene cation tetrakis[tris(dimethylamino)phosphoranylidenamino]phosphonium, which cannot form ylides.[10d]

Since only the ion pairs can propagate, the fraction of those is proportional to the observed polymerization rate, $\bar{k}_p = \alpha k_p$, where the fraction of ion pairs, α, is given by $\alpha = K/(K + 1)$, and $K = \exp(-\Delta G_{iso}/RT)$ is the equilibrium constant of the ylide/ion-pair isomerization. The intrinsic rate constant, $k_p \sim \exp(-1/a)$,[11] should not strongly depend on the nature of the counterion since the interionic distance, a, within the ion pair does not strongly differ for the various cations. For the same reason, the equilibrium constant of dissociation into free ions and solvent effects on the ylide/ion-pair equilibrium should be similar for all cations. Therefore, in this paper we did not take solvation energies into consideration. From the kinetics observed in the presence of the TPP cation, a fraction of ion pairs, $\alpha \approx 0.01$, was estimated at room temperature, corresponding to $K \approx 0.01$ and $\Delta G_{iso} \approx +11$ kJ/mol. The entropy changes for these

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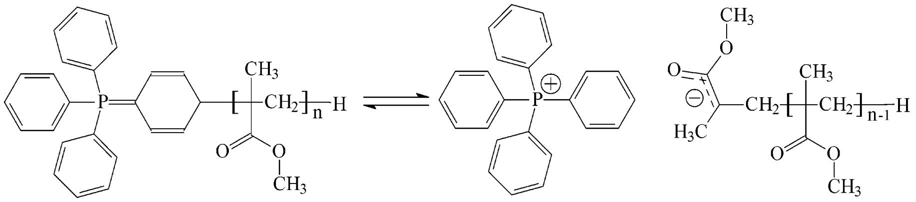
Scheme 1. Equilibrium between Ylides and Ion Pairs



unimolecular isomerizations are expected to be small, and it will be shown below that it is indeed so.

A clear trend was also observed for the observed activation energies, $E_{a,obs}$, of these polymerizations, which increase in the order $P_5^+ < PNP^+ < TPP^+$.[10c] This was explained by the fact that the energy of ion pair formation from the ylide, ΔE_{iso}, adds to the intrinsic activation energy, E_a, i.e., $E_{a,obs} = E_a + \Delta E_{iso}$:

$$P_5^+: \quad E_{a,obs} = E_a = 19.2 \pm 0.9 \text{ kJ/mol};^{10d} \quad \Delta E_{iso} = 0$$

$$PNP^+: \quad E_{a,obs} = 26.2 \pm 0.1 \text{ kJ/mol};^{10c} \quad \Delta E_{iso} = 7 \pm 1 \text{ kJ/mol}$$

$$TPP^+: \quad E_{a,obs} = 28.3 \pm 2.5 \text{ kJ/mol};^{10a} \quad \Delta E_{iso} = 9 \pm 3 \text{ kJ/mol}$$

Thus, for the $PMMA^-,TPP^+$ system, $\Delta E_{iso} \approx \Delta G_{iso}$ within the experimental accuracy, confirming the virtual absence of the entropic contribution into the ΔG_{iso} value estimated from the measured rate constant.

As both the polymerization rate and the activation energy are related to the energy difference between ylides and ion pairs the knowledge of this difference as well as its prediction for other systems is important. In this paper, we present the results of first-principles density functional theory (DFT) studies on the equilibrium between ylide structures and corresponding ion pairs for model of chain ends of the anionic polymerization of methyl methacrylate with different phosphonium countercations. Absolute energies of the ylides and ion pairs are calculated for a number of initiators, and the energy differences are correlated with the observed reactivity.

Methods of Computation

Density Functional Theory (DFT) Calculations. All density functional theory (DFT) geometry optimizations were performed using the parallel Karlsruhe TURBOMOLE[12] quantum chemistry package on a 12-processor SGI Power Challenge system and a 20 processor PentiumPro Cluster. A BP86[13] gradient corrected functional in the RI formalism[14] has been used throughout for the geometry optimizations. The energetics for the different stages of the insertion reaction has been checked by single-point calculations with a B3LYP− functional.[15] The numerical integration scheme employed using a "m3"-grid has been described in ref 16. For the fitting of the Coulomb-potential within the RI-formalism, Ahlrichs auxiliary basis sets[14b,17] have been used. The geometry optimizations have been carried out using a *split valence* (SV) (7s3p)/[3s2p] basis augmented with a d-polarization function (exponent 0.8) for carbon and oxygen (d-exponent 1.2), a *double*-ζ (6s)/[2s] basis set for hydrogen and a *split valence* (SV) (11s7p)/[6s4p] basis set for phosphorus with one additional d-function (exponent 0.45). This basis (which is comparable to a 6-31G*) is referred to as SV(P).[18]

For the single-point energy calculations with the B3LYP functional, a larger basis set named TZV(P)[19] has been used for C, O, H, and P. This basis set is of *triple*-ζ quality for the valence shells. The polarization functions are as described above, the contraction patterns are (5s)/[3s] for hydrogen (again, the (P) denotes polarization functions everywhere except on H), (11s6p)/[5s3p] for carbon and oxygen and (14s9p)/[5s4p] for phosphorus. The basis sets are accessible through WWW.[20] As in standard nomenclature, a B3LYP/TZV(P)//BP86/SV(P) denotes a single-point energy calculation with a B3LYP functional employing the TZV(P) basis at a geometry optimized with a BP86 functional obtained with a SV(P) basis.

The approach described above has been successfully employed by us for studying the structures and relative stabilities of different forms of anionic chain ends.[21] Its rms error for the energies of a large variety of molecules is about 17 kJ/mol.[22] Thus, it is much more reliable than semiempirical methods similar to AM1 which gives the rms error of ca. 80 kJ/mol.[22]

Results and Discussion

The apparent reactivity of a given chain-end may be estimated from the relative stability of its active ion pair form with respect to its dormant ylide form, being characterized by the values of isomerization reaction energies, ΔE. Table 1 presents the calculated ΔE values for the isomerization of ylides into the corresponding ion pairs, consisting of different phosphonium cations and the model anionic chain end of PMMA (nos. 1−3) or poly(methyl acrylate) (no. 4) with one ($n = 1$) or two ($n = 2$) units. The most reliable data are those obtained at the B3LYP/TZV(P)//BP86/SV(P) level (see, e.g., ref 22 for a comparison of functionals).

It should be noted that the structures under investigation contain fragments of acrylate and methacrylate chains which may adopt many different conformations. Although it was impossible to perform a complete conformational analysis, we have found and presented the conformations minimizing steric interactions in the spatial regions between (meth)acrylate chains and phosphonium counterions. The conformations of chain tails distant from counterions could be not optimal, but they are the same in ylides and ion pairs. Thus, possible errors in absolute total energies of ylides and ion pairs are canceled to a considerable extent in the ΔE values.

The character of stationary points was checked for two structures presented in Figure 2b,d. They are local minima having no imaginary vibrational frequencies. Zero point vibrational energies and thermal and entropy corrections calculated at the BP86/SV(P)//BP86/SV(P) were combined with the ΔE values calculated at the B3LYP/TZV(P)//BP86/SV(P) level. Resulting values of reaction enthalpy, ΔH, entropy, ΔS, and free energy, ΔG, for the isomerization reaction of the ylide (Figure 2b) into the ion pair (Figure 2d) are presented in Table 2.

It may be seen from Table 1 that our calculations correctly reproduce the experimentally observed relative reactivities of PMMA anionic chain ends in the presence of different phosphonium cations: the ΔE values for the PNP systems, Figure 1, (no. 1, $\Delta E = 20.7$ kJ/mol for $n = 1$ and -12.9 kJ/mol for $n = 2$ at the B3LYP/TZV(P)//BP86/SV(P) level) is considerably lower than those for the TPP systems, Figure 2, (no. 2, $\Delta E = 40.8$ kJ/mol for

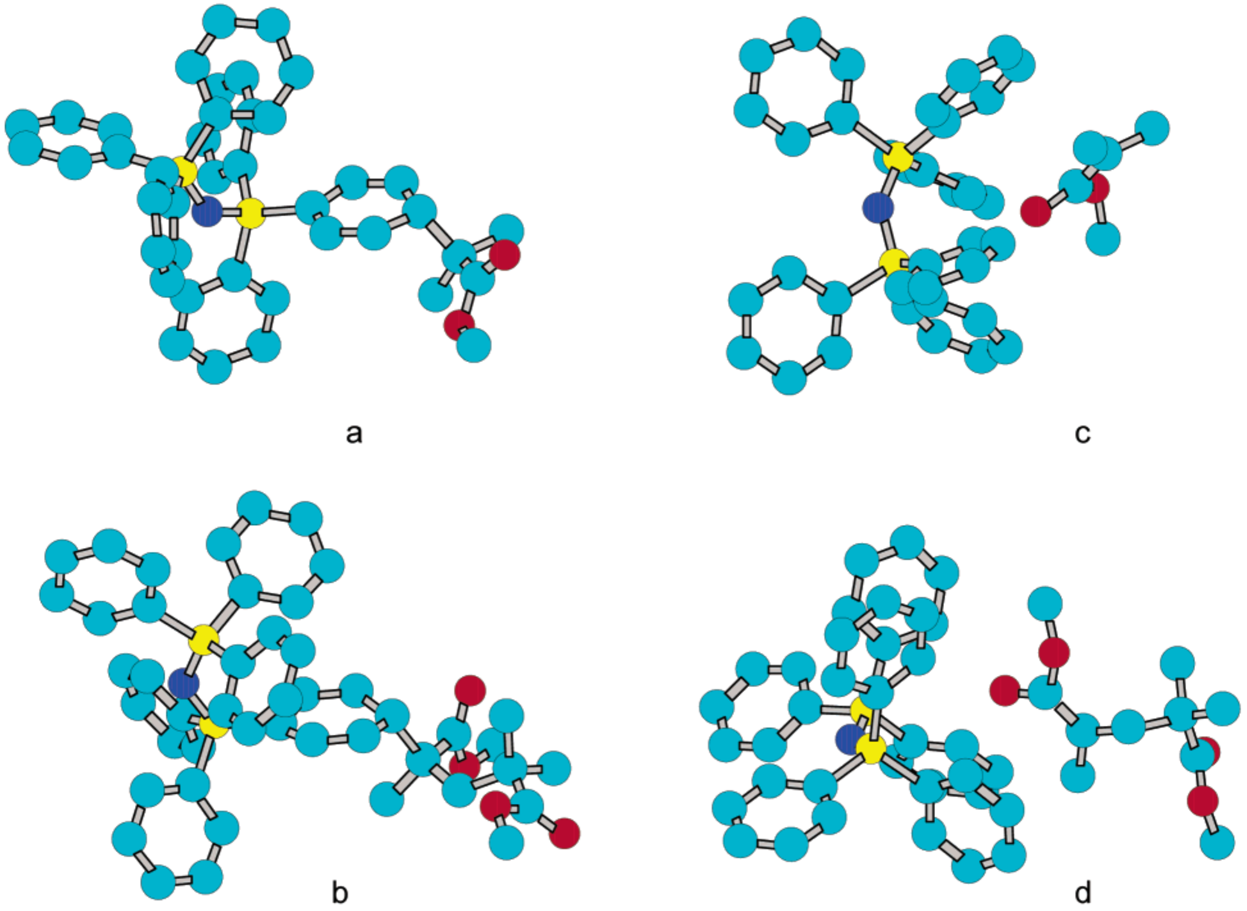
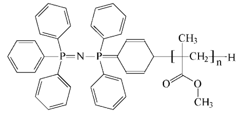
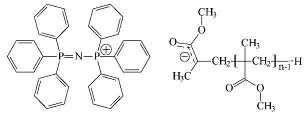
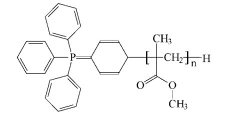
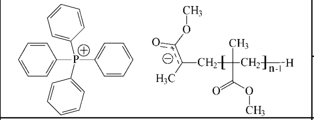
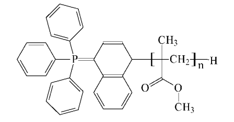
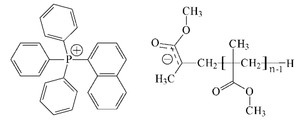
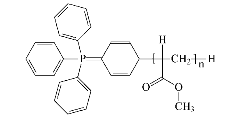
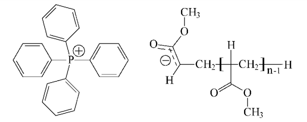
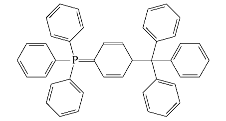
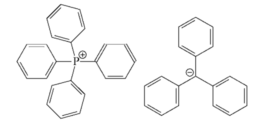


Figure 1. Optimized structures of the ylide (a, b) and ion pair (c, d) forms of the PNP, (polymethacrylate anionic chain end) systems for $n = 1$ (a, c) and $n = 2$ (b, d) (hydrogen atoms are not shown).

Table 1. Energies, Δ*E*, of the Isomerization of Ylides to Ion Pairs, Calculated at the BP86/SV(P)//BP86/SV(P) and B3LYP/TZV(P)//BP86/SV(P) (Marked Bold) Levels of Theory

no.	Ylide structure	n	Fig	Ion pair structure	n	Fig	ΔE, kJ/mol
1		1	1a		1	1c	34.6 **20.7**
		2	1b		2	1d	8.7 **-12.9**
2		1	2a		1	2c	42.6 **40.8**
		2	2b		2	2d	6.3 **-4.5**
3		1	3a		1	3c	77.3 **76.2**
		2	3b		2	3d	21.0 **11.0**
4		1	4a		1	4c	48.5 **47.1**
		2	4b		2	4d	30.0 **14.3**
5		-	-		-	-	-17.9 **-20.9**

$n = 1$ and −5.7 kJ/mol for $n = 2$). The rather high positive value of Δ*E* for the TPP−(methyl isobutyrate) system (Table 1, no. 2, $n = 1$) agrees with the induction period observed in the polymerization of MMA initiated by TPP, methyl isobutyrate.[10a]

One may also see from Table 1 that the isomerization energies for the NTP systems, Figure 3, (no. 3, Δ*E* = 76.2 kJ/mol for $n = 1$ and 11.0 kJ/mol for $n = 2$ at the B3LYP/TZV(P)//BP86/SV(P) level) are much higher than those for the TPP systems. This agrees with the fact

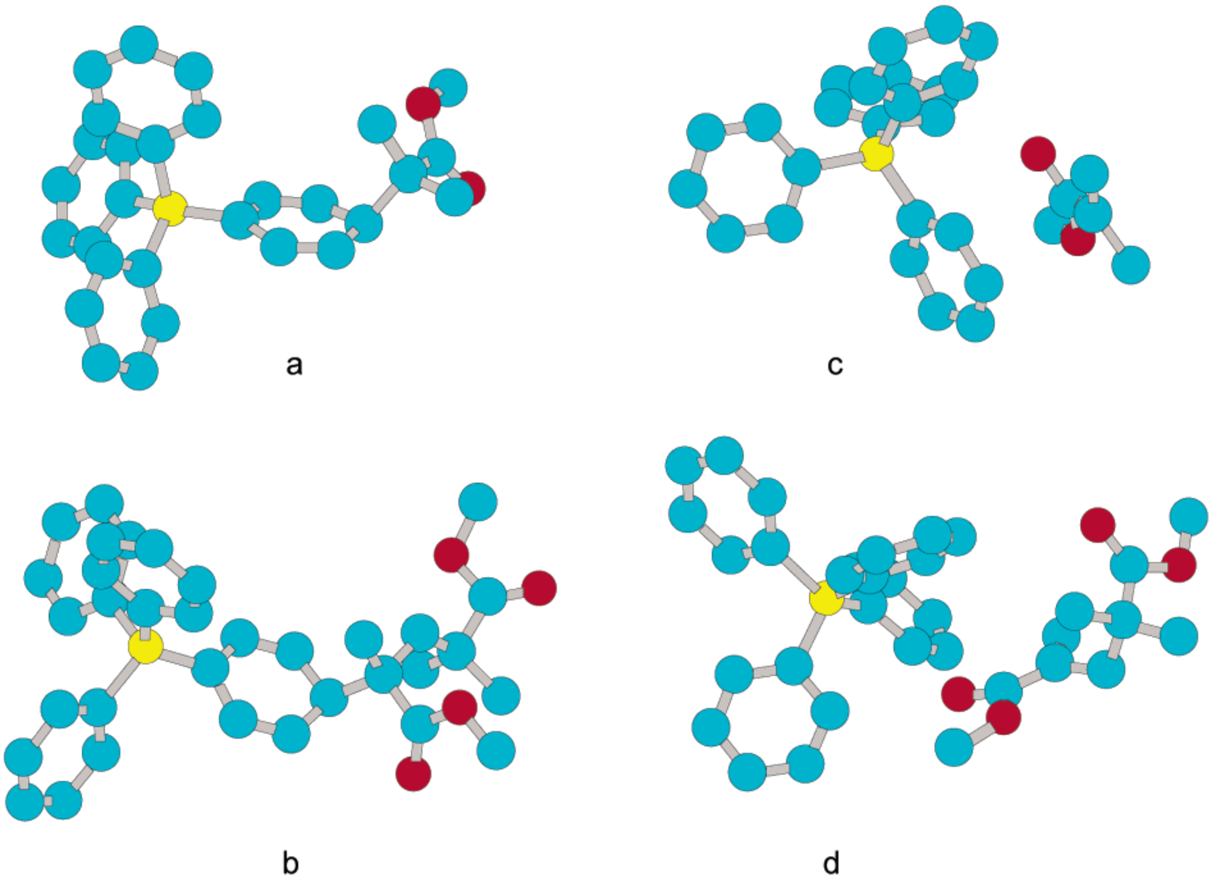


Figure 2. Optimized structures of the ylide (a, b) and ion pair (c, d) forms of the TPP, (polymethacrylate anionic chain end) systems for $n = 1$ (a, c) and $n = 2$ (b, d).

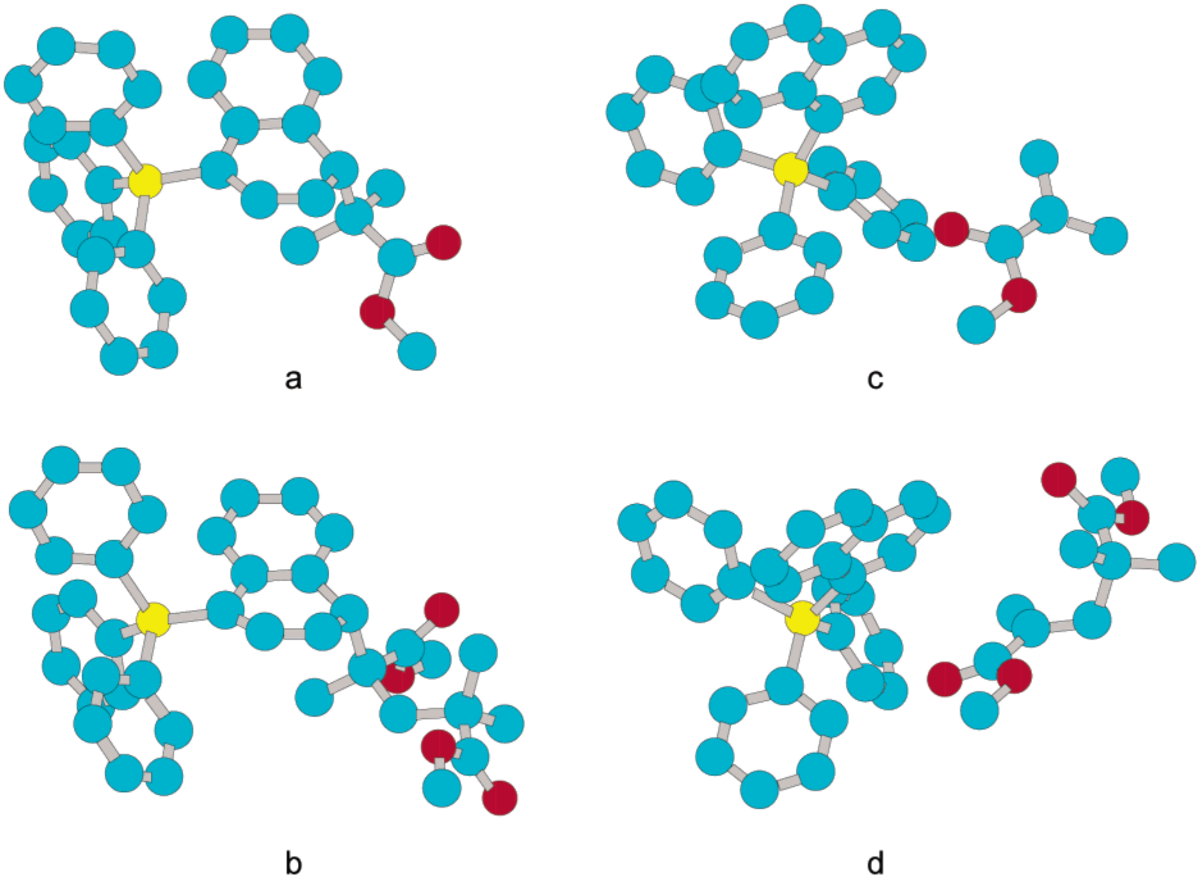


Figure 3. Optimized structures of the ylide (a, b) and ion pair (c, d) forms of the NTP, (polymethacrylate anionic chain end) systems for $n = 1$ (a, c) and $n = 2$ (b, d).

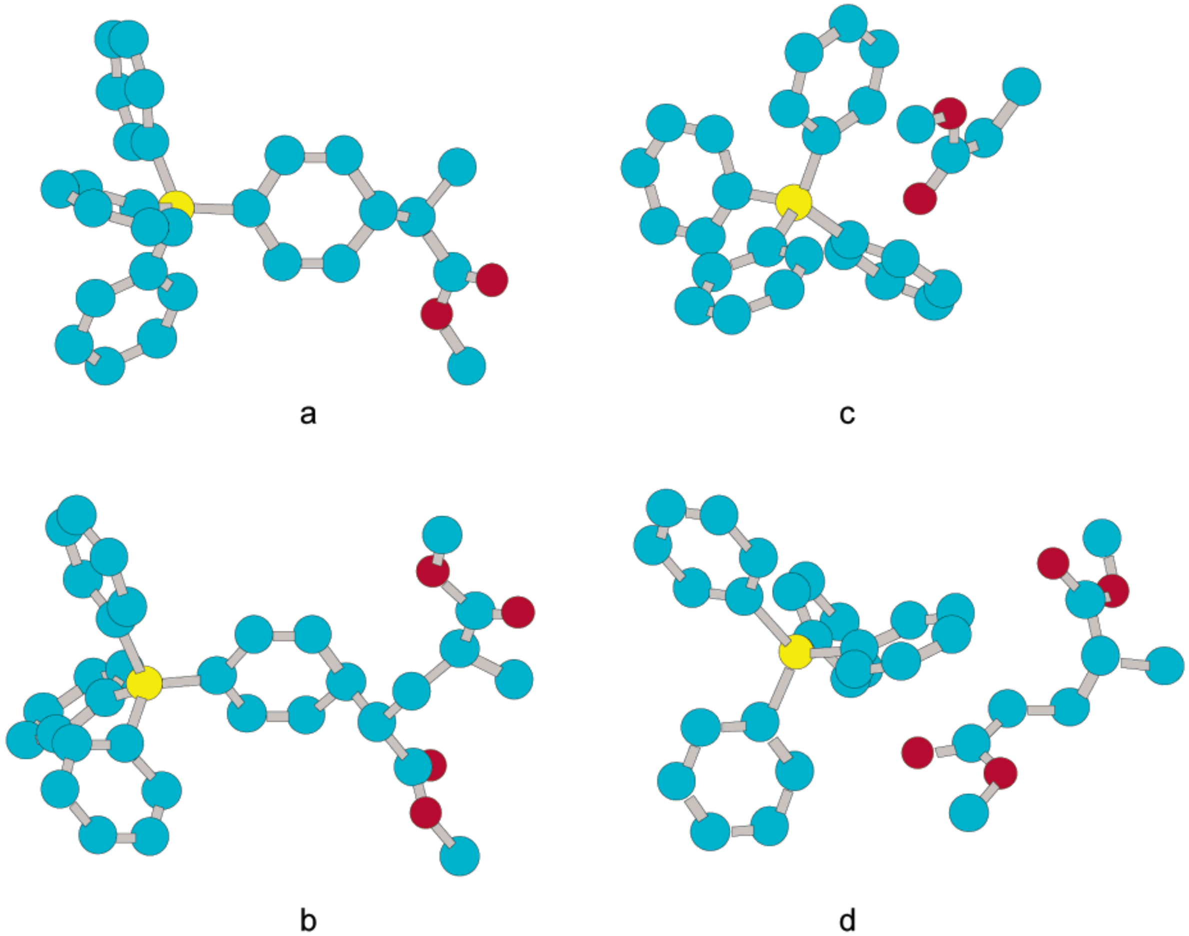


Figure 4. Optimized structures of the ylide (a, b) and ion pair (c, d) forms of the TPP, (polyacrylate anionic chain end) systems for $n = 1$ (a, c) and $n = 2$ (b, d).

Table 2. Calculated Enthalpies, ΔH, Entropies, ΔS, and Free Energies, ΔG, of the Isomerization of the Ylide (Figure 2b) to the Ion Pair (Figure 2d)

temp, °C	ΔH, kJ/mol	ΔS, J/(mol·K)	ΔG, kJ/mol
0	−9.8	−11.1	−6.8
20	−9.7	−10.6	−6.5
40	−9.5	−10.2	−6.3
60	−9.4	−9.9	−6.1
80	−9.3	−9.6	−5.9
100	−9.3	−9.4	−5.7

that the MMA polymerization in the presence of the NTP$^+$ counterion is by orders of magnitude slower than with TPP$^+$.[9b,c]

The data presented in Table 1 show that the stability of ion pairs with respect to ylides and, consequently, the reactivity of chain ends should increase with n. This finding is corroborated by the observation that a solution of PNP$^+$, ethyl isobutyrate$^-$ (the model of the active chain end) has an orange-red color indicating a considerable amount of dormant ylides, whereas the PNP$^+$, PMMA$^-$ growing polymer is colorless indicating a low ylide content.[10c] Thus, increasing the steric hindrance of the anionic fragment destabilizes the ylide structure with respect to the ion pair form. The same effect was calculated for the TPP, triphenylmethanide system containing the sterically crowded triphenylmethanide anion (Table 1, no. 5, $\Delta E = -20.9$ kJ/mol at the B3LYP/TZV(P)//BP86/SV(P) level), which is in agreement with the fast initiation of MMA polymerization by this initiator.[9a]

When the data for the TPP systems with methacrylate and acrylate anionic chain ends are compared, it is clear that the isomerization of ylides into corresponding ion pairs is much less favorable in the case of acrylates, Figure 4 (Table 1, no. 4, $\Delta E = 47.1$ kJ/mol for $n = 1$ and 14.3 kJ/mol for $n = 2$ at the B3LYP/TZV(P)//BP86/SV(P) level), than in the case of methacrylates. This result is easily explained by the decreased steric strain of the acrylate group with respect to the methacrylate one; it is also confirmed by kinetic data showing a much lower polymerization rate for acrylates with TPP$^+$ counterion.[23]

As seen from Table 2, the entropy, ΔS, for the izomerization of ylides to ion pairs is indeed small as expected. The negative sign of ΔS is explained by the fact that the ylide has very soft vibrational modes while the ion pair is smaller and more rigid. The ΔG values (−6.8 to −5.7 kJ/mol, Table 2) do not differ considerably from the ΔE value (−4.5 kJ/mol, Table 1). The difference between the calculated ΔG values (−6.5 kJ/mol at room temperature, Table 2) and that estimated from kinetic data[10a] (+11 kJ/mol) is about 17 kJ/mol which is typical rms error of B3LYP calculations.[22] The most important result is that one may predict the qualitative effect of the counterion structure on the polymerization rate constant, comparing the ΔE values for the corresponding reactions of izomerization of ylides to ion pairs.

Conclusions

The DFT calculations carried out in the present study qualitatively agree with the experimental findings[9,10] on the relative reactivities of metal-free initiators containing different cations of phosphonium type. It is shown that the isomerization of ylides to ion pairs may be rather endothermic in the initiation step, in qualitative agreement with induction periods observed during metal-free anionic MMA polymerization with phosphonium counterions.[10a] However, the next propagation steps are much more favorable, because the growing polymer chains in their ylide form are much more sterically demanding than the original initiators and, therefore, destabilize the dormant ylide structures compared to active ion pairs.

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Supporting Information Available: Tables of calculated absolute total energy values, *E* (in hartrees), at the BP86/SV(P)//BP86/SV(P) and B3LYP/TZV(P)//BP86/SV(P) levels, and of the BP86/SV(P)-optimized Cartesian coordinates (in Å) and input files for visualization with the HYPERCHEM software (extension .hin) for all the structures presented in Figures 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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