ELSEVIER

Polymer 42 (2001) 1915–1920

polymer

www.elsevier.nl/locate/polymer

Ab initio calculation of the rate coefficient for short-chain branching in free-radical polymerizations

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Received 26 June 2000; accepted 10 July 2000

Abstract

Short-chain branching in polyethylene, which involves a six-centre transition state, is studied by ab initio quantum mechanics up to the QCISD(T) level. The calculation gives a (low-pressure) activation energy of 73 kJ mol^{-1} and a frequency factor of 4.8×10^{12} s^{-1}. The frequency factor for this six-centre transition state is expected to be of acceptable accuracy and also applicable to homologous systems, such as short-chain branching to polymer in acrylates. These results overestimate the amount of ethylene short-chain branching observed in experiment, but the discrepancy is within the uncertainties of both experiment and calculation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ab inito calculations; Free-radical polymerization; Short-chain branching

1. Introduction

The amounts of long-chain (LCB) and short-chain branching (SCB) have major effects on the physical properties of polymers, including polyethylene, poly(alkyl acrylates), poly(vinyl acetate), and polyisoprene [1–6]. However, rate coefficients of the possible reactions involved have proved difficult to obtain, because it is hard to study the various possible reactions in isolation. It is now possible to use ab initio quantum mechanics to calculate information about these rate coefficients with sufficient accuracy to be of semi-quantitative use in understanding and control of these processes, using methods recently developed to take proper account of the transition states in free-radical polymerization reactions [7–9]. In particular, using these methods it is possible to calculate frequency factors with quite acceptable accuracy with relatively low-level quantum chemistry calculations.

The short-chain branching reaction is shown in Fig. 1. Importantly, because of the similarities between the transition states, quantum calculations of this type for the *frequency factor* for short-chain branching in the polyethylene free-radical polymerization studied here will give a result that will be both applicable to, and reliable for, the same process in acrylates such as butyl acrylate [10] (unless there is a dramatic difference in hindered rotations in the transition state between acrylates and ethylene). This can be particularly useful in modelling the branching process in such monomers (e.g. Ref. [11]). Modelling often may be the best way of estimating the various amounts of long- and short-chain branches: one can use this theoretical frequency factor together with an experimental activation energy found either for another reaction in a given homologous series or for homologous small-molecule reactions. This is because accurate experimental data for the propagation rate coefficient obtained by pulsed-laser polymerization (PLP) for the methacrylates [12–15], together with quantum mechanical studies of the appropriate transition states [9], suggests that the homologous-series procedure should give frequency factors for such processes that are accurate within (say) a factor of 2.

A summary of the reactions currently thought to be of possible significance in branching in polyethylene is given in Fig. 2. In 1953, Roedel [16] proposed a ‘back-biting’ reaction to explain butyl branching, involving intramolecular chain-transfer via a six-centre transition state (Fig. 1). Wilbourn [17] suggested that further propagation and back-biting would lead to ethyl branches, which would result in 2-ethylhexyl, 1,3-diethyl, tetrafunctional-dibutyl, and assorted even-carbon short branches. Roedel based his hypothesis on the physical properties of LDPE and

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PII: S0032-3861(00)00519-X

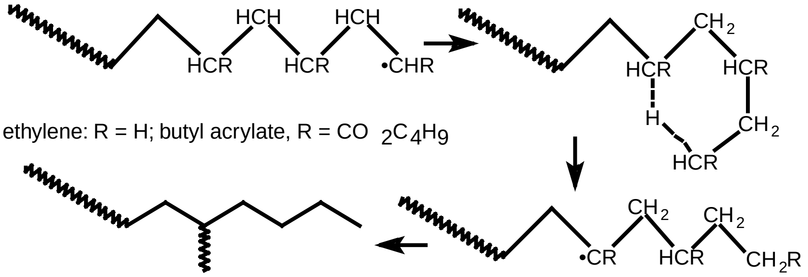

Fig. 1. Reactant, transition state and product for short-chain branching.

previous branching studies involving CH_3 composition. Further information came from ^{13}C NMR studies by Randall [18] and Bovey et al. [19]. Bovey et al. agreed with Roedel's hypothesis but questioned the mechanism for the existence of ethyl branches. It was noted that the probability of tetrafunctional dibutyl branches being created was enhanced by the increased reactivity of the branch-point hydrogen to a second-hydrogen extraction [20], as the tertiary radical formed is more stable. Dorman [21] used ^{13}C NMR, and Blitz [20] used FTIR to conduct studies agreeing with Roedel's hypothesis, finding branching ratios (r_{bb}) of 12 and 16 per 1000 CH_2, respectively. Axelson [22] studied polyethylene using ^{13}C NMR and supported Roedel's mechanism; it was concluded that this Roedel's mechanism must be extended to accommodate the presence of ethyl branches, but Wilbourn's results and argument, which suggested in more ethyl than butyl branches, were deemed incorrect. Other studies have also supported the greater relative incidence of butyl branches. Stoiljkovich and Jovanovich [23] related branching type and frequency to entropy in high-pressure systems and proposed an alternative mechanism involving bi-radicals. Viswanadhan [24] addressed the problem using configurational statistics, concluding back-biting to be more likely for polyethylene than for poly(vinyl acetate).

Roedel's proposed back-biting mechanism seems the most plausible and best supported by experimental evidence. Knowledge of the frequency factor (A), activation energy (E_a) and volume of activation ($\Delta V^{\ddagger}$) for this reaction would allow prediction of branching levels at different synthesis conditions. The present paper gives the first

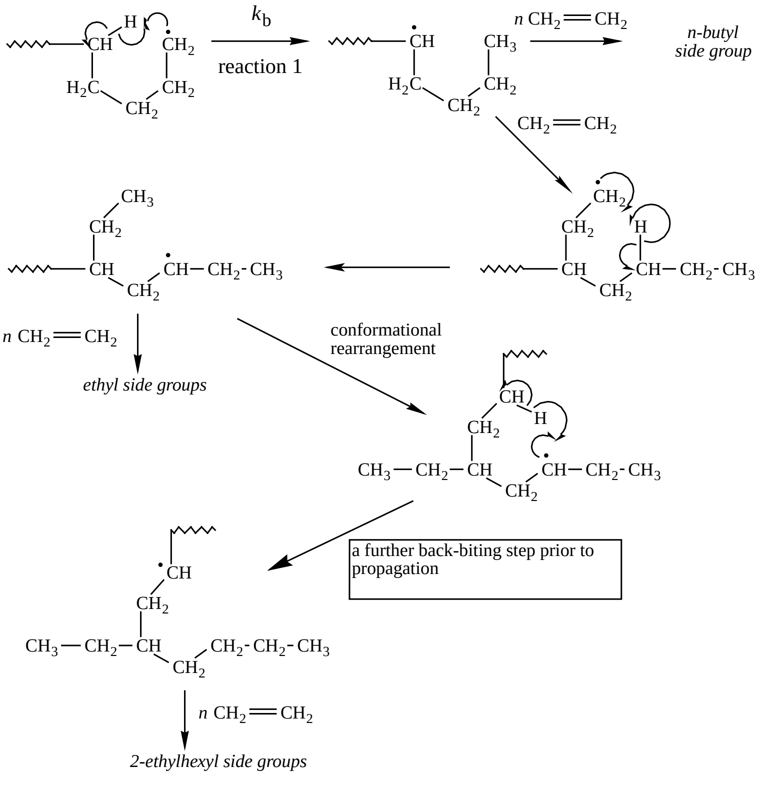

Fig. 2. Reactions thought to be of significance in polyethylene branching.

application of a method used to obtain the rate coefficients for free-radical polymerizations from ab initio quantum mechanical calculations of appropriate properties of reactant and transition state [7–9] to estimate A and E_a for the rate coefficient k_b of the initial reaction in the branching scheme. It is reiterated that the frequency factor so obtained will also be applicable to short-chain branching in analogous reactions as those of the acrylates, and that obtaining this frequency factor is the principal objective of this paper.

2. Method

The transition state expression for a unimolecular rate coefficient is (see, e.g. Ref. [25]):

$$k = \frac{m^{\dagger}\sigma}{m\sigma^{\dagger}} \frac{k_B T}{h} \frac{Q^{\dagger}}{Q} \exp(-E_0/k_B T) \tag{1}$$

where k_B is the Boltzmann constant, T the temperature, h is Planck's constant, Q and $Q^{\dagger}$ are the partition functions for reactant and the transition state (TS), respectively, E_0 the energy difference between the zero-point vibrational energy levels of the reactants and TS (note that E_0 is approximately but not exactly the activation energy [25]), and σ ($\sigma^{\dagger}$) and m ($m^{\dagger}$) are the symmetry numbers and number of optical isomers of reactant (transition state). Assuming separability of the molecular Hamiltonian, the partition function Q can be written as a product of translational, vibrational and rotational terms. Reaction (1) in Fig. 2 is a unimolecular process, and so the translational partition functions exactly cancel in Eq. (1). Because the polymer chain is essentially infinitely heavy, the rotational partition functions also cancel. The reaction path degeneracy term $m^{\dagger}\sigma/m\sigma^{\dagger}$ is unity for this system. One thus has:

$$\frac{Q^{\dagger}}{Q} = \Pi \frac{1 - e^{-h\nu_i}}{1 - e^{-h\nu_i^{\dagger}}} \tag{2}$$

where ν_i are the vibrational frequencies.

All ab initio calculations were carried out with GAUSSIAN 94 [26], for both a six-carbon and a seven-carbon chain. The latter should be sufficiently long to mimic an infinite chain, provided that frequencies are calculated by replacing an end-chain *trans* hydrogen with a heavy mass [8]. Geometries of both reactant and transition state were optimized from an initial guess from a Hartree–Fock calculation with a 3-21G (HF/3-21G) basis set. Due to the strain in the transition state, it was necessary to fix the transition state bond angle and lengths in a partial optimization, and then to optimize the result fully. Further optimization was performed at the HF/6-31G* level. Energies were calculated at both QCISDT/6-31G* and QCISDT/6-311G** levels. Scale factors of 0.8929 for frequencies and 0.9135 for zero-point energies were used [27]. Rate coefficients were calculated for a temperature of 200°C and 200 MPa pressure, conditions which are typical of those for which (limited) data are available for the amount of short-chain branching.

Accurate values of the Arrhenius frequency factor for this type of free-radical polymerization reaction require the lowest frequency vibrational modes to be replaced by hindered rotors whose torsional potential is obtained by energy calculations where the appropriate torsional angle is systematically varied [7,8]. However, this is a laborious process, and the improvement in accuracy (typically a factor of the order of 2 in the frequency factor) is not merited here.

There are at present no reliable means of calculating $\Delta V^{\ddagger}$ from a priori theory. The volume of activation for the unimolecular back-biting reaction is likely to be slightly negative, given the restricted nature of the transition state [28]. An upper bound to the magnitude of the effect of pressure can be found by assuming $\Delta V^{\ddagger} = -27\ \mathrm{cm^3\ mol^{-1}}$, as measured experimentally for ethylene free-radical propagation [29–31]. This value of $\Delta V^{\ddagger}$ predicts an increase of about a factor of 4 in the rate coefficient at 200 MPa above that at ambient pressure, suggesting that the pressure effects on the rate coefficient for reaction (1) are not likely to be large (and indeed will be to slightly decrease, not increase, k_b). Including $\Delta V^{\ddagger}$ with this value increases the calculated activation energy for short-chain branching by 5 kJ mol^{-1} at 200°C and 200 MPa. This has been added to all activation energies calculated from the quantum chemistry calculations (which of course are low-pressure values).

3. Results and discussion

Table 1 gives calculated critical energy values for the six- and seven-carbon transition states, with basis set size and level of theory increasing down the column. The geometry of the transition state is shown in Fig. 3. The vibrational frequencies of reactant and transition state, which give the frequency factor from Eqs. (1) and (2), are given in Table 2.

It can be seen that within the same level of theory (e.g. MP2 or PUHF), the energy differences between basis sets are about the same (e.g. ~10 kJ mol^{-1} for MP). In going from six to seven carbons, the critical energy decreases by about the same amount within similar theoretical treatments and regardless of basis set (e.g. ~13 kJ mol^{-1} for HF and PUHF, and ~17 kJ mol^{-1} for MP). Although there may seem to be a downwards trend in E_0 with increased level of theory, it must be realized that this energy is a difference in of two calculated energies and so does not have to decrease variationally.

The frequency factor shows convergence at a low level of theory, for reasons explained in detail elsewhere [8]. In brief, this is because: (a) the contributions to the frequency factor from frequencies significantly greater than $k_B T$ are negligible in Eq. (2); (b) many of the lower frequencies are similar in reactant and transition state, and so their contributions cancel in Eq. (2); and (c) the major contributions to the frequency factor come from hindered rotors, for

Table 1
Critical energies (kJ mol^{-1}) for 6-31G* and 6-311G** basis sets (the correction for volume of activation has not been added to these E_0 values, i.e. they are true critical energies)

Basis set	Level of theory	Critical energy	
		Six-carbon	Seven-carbon
6-31G*	HF	130.03	117.02
	MP2	83.69	67.51
	MP3	91.80	76.02
	MP4D	90.68	74.73
	MP4DQ	92.85	77.02
	PUHF	115.46	102.42
	PMP2	73.28	57.08
	PMP3	85.84	70.08
	MP4SDQ	88.88	72.90
	QCISD	86.65	70.71
	QCISDT	79.97	63.59
6-311G**	HF	128.99	116.18
	MP2	72.46	55.56
	MP3	82.12	65.83
	MP4D	80.53	*65*
	MP4DQ	83.69	67.35
	PUHF	114.67	101.83
	PMP2	62.21	45.30
	PMP3	76.36	60.08
	MP4SDQ	79.31	62.76
	QCISD	77.51	*69*
	QCISDT	69.07	*60 − 63*

which the partition function is dominated by geometrical considerations [25], and for which relatively low levels of quantum theory are adequate. The treatment used here may be expected [7,8] to yield a value of A which is within a factor of (say) 3 of the exact value, which is adequate for many purposes.

Computational limitations prevented QCISD/6-311G** and QCISDT/6-311G** calculations being performed on the seven-carbon species. Using the observed trends, however, energies for these levels of theory were estimated from the analogous six-carbon results and from the seven-carbon results at 6-31G* (given in italics in the table).

An explanation for the higher frequency factor for the seven-carbon model compared to that for the six-carbon one is the change in the terminal C–C–H angle between models. This angle is 3° larger for the seven-carbon model than in the six-carbon model. This is an expected result of adding a carbon atom, which results in different hindrance to rotation of the ring relative to the chain, and hence [9] reduces the partition function of the six-carbon transition state relative to the seven-carbon one. The same effect occurs with the bending of the chain towards the ring: the six-carbon partition function is less than that of the seven-carbon one. The combination of these two effects can explain the 10-fold higher frequency factor in the seven-carbon model.

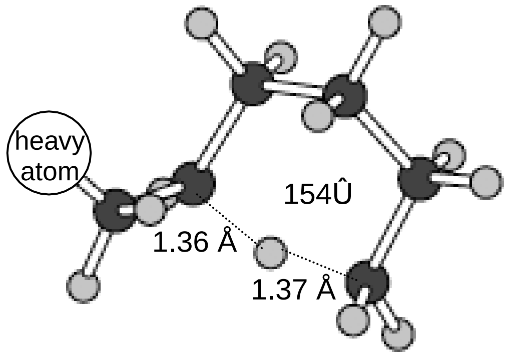

Fig. 3. Transition state geometry (HF/6-31G* level of theory) of the seven-carbon calculation.

Table 2
Frequencies of seven-carbon reactant and transition state (cm^{-1})

Transition state:
98, 108, 169, 248, 292, 330,
416, 447, 491, 556, 668, 814,
841, 888, 909, 943, 982, 1020,
1046, 1067, 1132, 1144, 1174,
1207, 1235, 1266, 1330, 1354,
1402, 1426, 1457, 1490, 1501,
1515, 1521, 1535, 1569, 1597,
1603, 1629, 1634, 1637, 1648,
1650, 1655, 3157, 3181, 3182,
3202, 3207, 3213, 3214, 3218,
3241, 3255, 3260, 3264, 3273,
3328

Reactant:
70, 80, 109, 142, 153, 169,
264, 265, 324, 438, 480, 522,
780, 791, 845, 927, 961, 990,
1066, 1084, 1119, 1138, 1148,
1151, 1219, 1265, 1337, 1374,
1396, 1438, 1446, 1456, 1461,
1506, 1549, 1566, 1569, 1602,
1628, 1634, 1635, 1641, 1644,
1651, 1658, 3134, 3177, 3178,
3187, 3191, 3194, 3198, 3200,
3205, 3222, 3238, 3259, 3260,
3307, 3404

Table 3 gives calculated values for the activation energy, frequency factor and branching ratio for the back-biting reaction at selected levels of theory. The relative butyl branching ratio (r_{bb}) is calculated from:

$$r_{bb} = 500 \frac{k_b}{k_p[M]} \tag{3}$$

(butyl branches per 1000 backbone CH_2 units)

where k_b and k_p are, respectively, the rate coefficients for back-biting and propagation, and [M] is the monomer concentration. The constant 500 is present because there are two CH_2 units per ethylene molecule, and hence 500 ethylene molecules react per 1000 CH_2 units. Values of r_{bb} are listed in Table 3 for 438 and 543 K, assuming a constant pressure of 200 MPa, and 15% conversion.

Note that Eq. (3) gives butyl branching per 1000

Table 3
Activation energies and amounts of short-chain branching. The activation energies incorporate an additional 5 kJ mol^{-1} to allow for the pressure dependence arising from the volume of activation (see text). "Long" and "short" refer to whether or not the "hydrogen" atom furthest from the radical centre is given a very high mass or a mass of 1 amu

	Chain length	E_a (kJ mol^{-1})	$\log_{10} A$ (s^{-1})	Butyl branching	
				543 K	433 K
Six-carbon					
UHF 6-31G*	Long	132.8	11.4	7.3×10^{-5}	3.0×10^{-7}
QCISD 6-31G*	Short	89.4	11.5	1.2	0.0
	Long	89.5	11.4	1.1	0.0
QCISDT 6-311G**	Long	71.9	11.4	54	6
Seven-carbon					
UHF 6-31G*	Long	124.6	12.7	8.0×10^{-3}	5.1×10^{-5}
QCISD 6-31G*	Long	78.3	12.7	229	17
QCISDT 6-31G*	Long	71.1	12.7	1124	122
Propagation	From theory [8]	33.3	7.1		

backbone CH_2 units, not per 1000 CH_2 units present, as is found experimentally. For example, with 20 butyl branches per 1000 CH_2 units, this represents 20 branches per 920 ($= 1000 - 4 \times 20$) backbone CH_2 units, less than a 10% difference.

4. Comparison with experiment

The main objective of this paper is to obtain the frequency factor for short-chain branching for ethylene, and hence by extension for acrylates as well. While the level of theory used is not sufficient to give a reliable activation energy, it is worthwhile making a comparison with experimental data for short-chain branching. Comparison with experiment is made difficult because there are no literature data available where the amount of branching has been determined with fixed temperature, pressure and conversion. Of the quantitative studies mentioned, butyl branching has been reported to vary from ~5 [19,21] to 16 [20] per 1000 CH_2, and the ratio Et/Bu has varied from 2 [17] to 0.2 [19]. However, these studies have all consistently found an absence of propyl branching and a low but detectable frequency of amyl branching. The experimental results quoted above have supported an extended back-biting hypothesis. Differences in results could be due to differences between NMR and IR sensitivities (although Blitz's comparison [20] finds little difference between each), but are more likely due to the different assumptions made in assigning resonances and bands to various branches.

One explanation for these apparent experimental differences is simply different synthesis conditions. It is therefore difficult to compare the calculated branching ratios with experiment. In the best-controlled experimental studies currently available, McCord et al. [32] synthesized LDPE in carefully controlled conditions: a well-mixed autoclave, 10–20% conversion, and pressure of about 10^2 MPa. They reported butyl branching ratios of 6 per 1000 CH_2 at 438 K and 20 per 1000 CH_2 at 543 K. Our value for branching at the highest level of theory used (QCISDT/6-31G*) gives $r_{bb} = 122$ per 1000 CH_2 groups at 438 K, and 1124 per 1000 CH_2 groups at 543 K. This suggests that Roedel's back-biting hypothesis is sufficient to explain butyl branch formation; however, these results are a factor of 20 and 50 higher than McCord's findings, and this large over-prediction needs to be explained.

For reasons discussed elsewhere [8], the means used here to calculate the frequency factor are likely to give good results, and the greatest uncertainty lies with the calculated activation energy. One possible problem may lie in the number of carbons used: the heavy atom does not allow for the lateral movement, which is possible when a long chain is present. A similar study on the homo-propagation of ethylene [8] found that the Arrhenius parameters vary with carbon additions until the macroradical mass was placed on the third carbon away from the transition site. The convergence in A was explained by the heavy mass having been placed far enough away from the axes of rotation, while E_a convergence occurs because the extra carbons are now added far enough from the transition site that they do not affect it. The approximation of treating vibrations as harmonic oscillators is unlikely to induce errors more than a factor of 2 in A and negligible error in E_a [8].

An increase of E_a by 10 kJ mol^{-1}, which from Table 3 is a reasonable estimate for the uncertainty in this calculated quantity, would result in an order of magnitude decrease in r_{bb}. A decrease in A by a factor of up to 2–4, expected from previous studies to accompany a longer-chain model, would decrease branching predictions in line with experiment.

Further back-biting reactions not considered here might also reduce the number of butyl branches, replacing some of them with ethyl and ethyl–hexyl branches. The potential for altered reactivity at a branch point would need to be considered if this were added to the model, and the higher reactivity of tertiary compared to secondary hydrogens to abstraction is noted [33]. Also not addressed are possibilities of other reactions which result in short-chain branching, the most likely being seven- or five-membered transition states leading to amyl and propyl groups, respectively. It is expected from experiment [18,19] that when such reactions are examined theoretically, the activation energy of the former will be lower than the latter, although higher than that for the six-membered ring. This might explain the absence of propyl branching and the low amyl branching found by experiment.

5. Conclusions

The calculations given here should provide reliable frequency factors for short-chain branching in ethylene free-radical polymerization, and also be of moderate accuracy for the same process in acrylates. Although the predicted amounts of SCB are much higher than experiment, the discrepancy may be ascribed to reasonable errors in the activation energy; however, improvements in both calculations and experiment are needed to resolve this.

Acknowledgements

The authors gratefully acknowledge the support of the Australian Research Council both for an Institutional Grant and through the establishment and support of the Key Centre for Polymer Colloids.

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