Pulsed-Laser Radical Polymerization and Propagation Kinetic Parameters of Some Alkyl Acrylates

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SUMMARY: Pulsed-laser photoinitiated polymerization was used to determine, in toluene solution, the propagation kinetic parameters of a series of acrylates with increasing size of the alkyl side group. Transfer to monomer and to toluene did not occur significantly in our PLP conditions and our temperature range since no broadening of the MMD was observed, allowing generally to work with two inflection points. In contrast, depending on the nature of the acrylate and on the PLP conditions, transfer to polymer, and thus long chain branching, can critically interfere. Indeed, the Mark-Houwink-Sakurada parameters, which are used to calculate the absolute molar mass at the inflection point, strongly depend on the polymer structure and thus, should be carefully measured for each PLP sample. Although still preliminary, the results show that the k_ps measured in toluene solution present a tendency to continuously decrease when increasing the size of the side group. This observation is conflicting with the reported behaviour for PLP experiments in bulk, revealing a possible solvent effect.

Introduction

We recently joined the Working Party “Modeling of Polymerization Kinetics and Processes“ of the IUPAC Macromolecular Division which gathers the efforts of different laboratories to determine the most credible kinetic parameters in radical polymerization. The rather new technique of pulsed laser photoinitiated polymerization (PLP)1) appears as the most confident and the IUPAC Group already published its results concerning styrene and some alkyl methacrylates2-4). We decided to focus on the series of *acrylates* which are presently considered by the Group. First results were already reported by the different partners concerning essentially the *n*-butylacrylate, and more partly the methyl, ethyl, 2-ethylhexyl and dodecyl acrylates5-11). It appears clearly that the high polymerization rates observed for the acrylate series makes the PLP approach less reliable than for styrene or methacrylates, and the much higher propagation rate constants observed in PLP with respect to conventional techniques (for example, rotating sector) need to be confirmed.

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After benchmarking our equipment with styrene polymerization, we undertook the PLP determination of k_p over a wide temperature range for a series of alkylacrylates either already considered by the Group (n-butyl, 2-ethylhexyl, ethyl) or newly examined (i-butyl, t-butyl, nonyl). We comment here about these experiments and results, either separately or within the framework of the IUPAC Working Party.

Experimental Part

Materials

Ethyl, n-butyl, i-butyl, t-butyl, 2-ethylhexyl, nonyl acrylates (purity ≥ 99.5 %, stabilized by 20 ppm of 4-methoxyphenol) were used as provided by Atofina. Monomer solutions in toluene containing 5 10^{-3} mol L^{-1} of photoinitiator, either benzoin (Prolabo) or more generally 2,2-dimethoxy-2-phenylacetophenone-DMPA (Aldrich), were carefully deoxygenated by flushing the cell with nitrogen before polymerization.

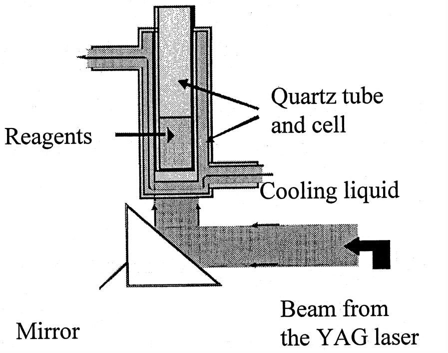


Fig. 1: Polymerization cell.

Polymerization

Photopolymerizations were performed from -30 to +50°C in toluene solution ($[M]_o = 1.5$ to 4.7 mol L^{-1}) using a thermoregulated cylindrical quartz cell with an inner diameter of 8 mm equal to the diameter of the beam (Fig. 1) in order to get a homogeneous irradiation. No stirring was used. The pulsed laser was a variable frequency Q-switched Nd:YAG (Quantel YG980S) with 2 crystals (SHG and THG) generating a beam at 355 nm with a maximum energy of 70 mJ/pulse. The frequencies were 100, 50, 20, 10 Hz and the pulse duration was 10-12 ns. Runs of 100 to 900 pulses led to monomer conversions ranging from 0.1 to 3%. Temperature was measured inside the cell with an accuracy of ± 0.1°C. For most experiments overall temperature increase did not overpass 2°C and was generally much lower. The reaction medium was directly analyzed by SEC and conversions were determined using the RI chromatogram and the refractive index increment (dn/dc). Monomer densities vs temperature and dn/dc at 30°C were determined for the whole series of polyacrylates.

Molar Mass Determination

Molar masses were measured using a triple detection (TD-SEC) equipment composed of a Waters 515 pump equipped with a Gastorr 102 outgasser, a Viscotek S5200 auto sampler, 3

Shodex columns KF 802.5L/804L/805L, a Viscotek 200 differential refractometer-viscosimeter, a Wyatt mini-Dawn light scattering detector, and the Viscotek TriSEC 3.0 software. Eluent was THF at 30°C. The refractive index increments and the Mark-Houwink-Sakurada coefficients (K, α) were either measured by triple SEC or taken from literature. Molar masses were determined from the RI chromatogram, using polystyrene calibration and the MHS parameters of the considered polymer. Inflection point of low MM side of MMD peaks was used for molar mass determination, as recommanded by Olaj et al$^{12)}$.

Benchmarking with Styrene Polymerization

Reference experiments were conducted both in bulk and in toluene solution between 25 and 70°C (Fig. 2 and 3). The frequency (10, 20, 50 Hz), pulse energy (5 to 30 mJ) and number of pulses per run were systematically varied. In all cases the conversions were low enough to avoid any significant increase of temperature ($\Delta T < 0.5$°C). Variations of styrene and toluene densities with temperature (°C) were taken into account, using data from literature ($d_{st} \sim 0.9236 - 8.87\ 10^{-4}\ T$ and $d_{tol} \sim 0.88575 - 9.41\ 10^{-4}\ T$)$^{6,13)}$. Molar mass determinations were performed over 39 runs, using the calibration curve obtained from PS standards (Viscotek), and the following relationship for k_p vs 1/T was obtained for bulk polymerization (298K< T <343K):

$$k_{p,bulk} = 10^{7.71 \pm 0.06}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(- \frac{32.7 \pm 0.4\ kJ \cdot mol^{-1}}{R \cdot T} \right) \qquad (1)$$

The linear least square regression was used and relative errors are based on the spread of the data observed for several runs at each temperature.

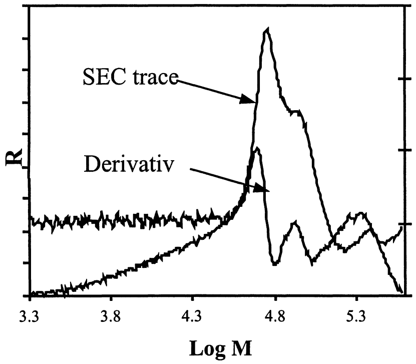


Fig. 2: Molar mass distribution (MMD) of the polystyrene formed in a bulk PLP experiment at 70°C, 10 Hz, 30 mJ/pulse, 600 pulses.

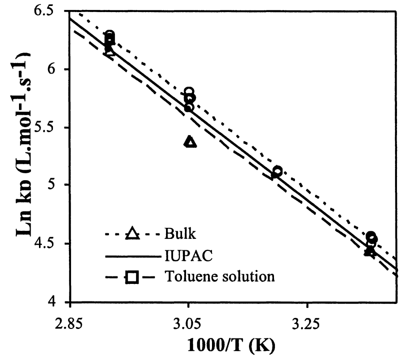


Fig. 3: Arrhenius plots for k_p obtained bulk and in toluene solution, and comparis with the plot reported by the IUPAC Grou

Comparison with the relation reported by the IUPAC Group for bulk polymerization[2)],

$$k_{p,\mathrm{bulk,IUPAC}} = 10^{7.630}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(- \frac{32.51\ kJ \cdot mol^{-1}}{\mathrm{R} \cdot \mathrm{T}} \right) \qquad (2)$$

shows that our activation parameters are in close agreement and that our equipment and our working conditions are reliable.

In toluene solution the observed A_p and E_A appear slightly lower but the number of runs was limited to 9 and the standard deviations are much larger than for bulk:

$$k_{p,\mathrm{tol}} = 10^{7.54 \pm 0.50}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(- \frac{32.1 \pm 3.1\ kJ \cdot mol^{-1}}{\mathrm{R} \cdot \mathrm{T}} \right) \qquad (3)$$

Results and Discussion

Some data on PLP of acrylates were already reported by the different teams participating to the IUPAC Working Party, and concern the methyl[6,11)], ethyl[7)], n-butyl[6,8,9,10)], 2-ethylhexyl[9)] and dodecyl[9,11)] esters. Most of the results were obtained in bulk except for n-butyl acrylate which was also examined in THF, toluene, super critical CO_2 solutions, and it appeared in fact difficult to get systematic correlations between the different sets of kinetic parameters and the structure of the monomers. The purpose of the present work was to reexamine (or examine), using the same device and same experimental conditions, series of acrylates either with linear side groups of increasing lengths (ethyl, n-butyl, nonyl) or with side groups of different bulkiness (n-, i-, t-butyl, 2-ethylhexyl). All polymerizations were performed in toluene solution within the [-30, +50°C] temperature range. The variations of monomer densities with temperature were determined from 5 to 50°C and appeared very close to linearity; thus we systematically considered that the linear regression relationship was a correct approximation to extrapolate the densities over the considered polymerization temperature range (T °C):

$d_{EA} = 0.94331 - 0.00111\ T$

$d_{n\text{-}BuA} = 0.91771 - 0.00095\ T$

$d_{i\text{-}BuA} = 0.90840 - 0.00097\ T$

$d_{t\text{-}BuA} = 0.90382 - 0.00103\ T$

$d_{EHA} = 0.90056 - 0.00081\ T$

$d_{NA} = 0.89420 - 0.00077\ T$

Ethyl Acrylate

The PLP of this monomer was studied at 100 Hz from -30 to +30°C. The kinetic parameters (Fig. 4-5) were obtained from 52 runs of 200 to 3600 pulses. The refractive index increment and then MHS coefficients were measured at 30°C in THF,

$$dn/dc = 0.073 \pm 0.004 \text{ mL mg}^{-1} \qquad K = 5.68 \pm 0.25\ 10^{-5} \text{ dL g}^{-1} \qquad \alpha = 0.774 \pm 0.004$$

These values of MHS parameters appear much closer to the ones reported by Penzel and Goetz14) than to those reported by Hutchinson et al15) and even than to the intermediate estimates used by de Kock7).

Varying the monomer concentration (from 3.5 to 4.7 mol.L^{-1}), the nature (DMPA or benzoin) and concentration of photoinitiator, the pulse energy (8 to 35 mJ), and the frequency (20 and 50 Hz below -15°C) led to same values of k_p and activation parameters observed at 100 Hz. The linear regression (243 < T < 283 K) leads to,

$$k_{p,EAl} = 10^{7.56 \pm 0.06}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(-\frac{19.27 \pm 0.37\ kJ \cdot mol^{-1}}{R \cdot T} \right) \text{ and } k_{p,EA}(20°C) = 13400 \text{ L mol}^{-1} \text{ s}^{-1}$$

Using the MHS parameters proposed by de Kock to retreat our SEC data (Fig 5) leads to rather close values of k_p even if the activation energy appears somewhat higher (20.09 ± 0.34 kJ mol^{-1}).

A scattering of the data together with a levelling off of $\ln k_p$ is observed above 13 °C, indicating that 100 Hz is most probably a too low frequency to avoid any transfer to toluene or monomer and then to get confident k_p values in the temperature range usually used in radical polymerization of acrylates.

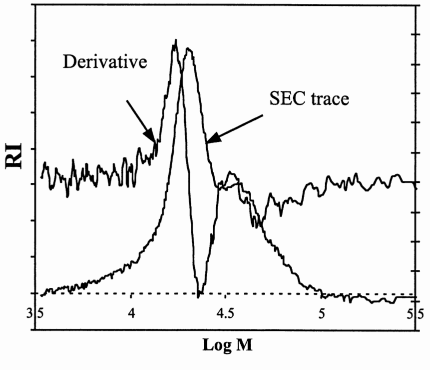


Fig. 4: Molar mass distribution (MMD) of polyethylacrylate formed in a PLP experiment in toluene solution at -20°C, 100 Hz, 27 mJ/pulse, 300 pulses.

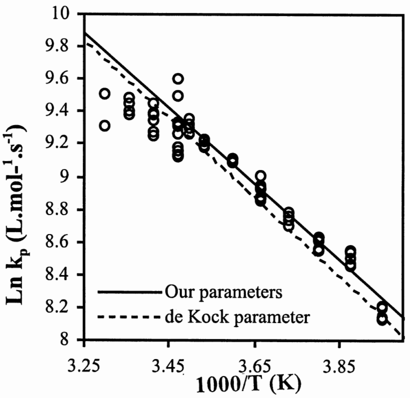


Fig. 5: Arrhenius plots for k_p obtained in toluene solution for various $[M]_o$ at 20, 50 and 100 Hz. The two plots correspond to the two sets of MHS parameters (see text).

Butyl Acrylates

The polymerizations of the three butyl acrylates were studied in toluene solution ($[M]_o$ = 1.75 to 2.5 mol L^{-1}) between -30 and 0°C. We did not determine yet their MHS parameters using the triple detection SEC, and the values previously reported in literature were used for MM determination. Series of 15 (n-BA), 32 (i-BA) and 50 (t-BA) runs with 300 to 600 pulses were performed (Fig. 6). The maximum conversion observed was 2.4 %, but most generally conversions for the exploited experiments ranged from 0.2 to 1 %.

In the case of n-butyl acrylate, we preferred the MHS parameters measured by Beuermann et al ($K = 12.2\ 10^{-5}$ dL g^{-1}; $\alpha = 0.700$)9) to those of Penzel and Goetz14), as recently Schmitt, using narrow MMD linear polymers prepared via living anionic polymerization, obtained values much closer to the first ones ($K = 11.8\ 10^{-5}$ dL g^{-1}; $\alpha = 0.716$)16). This might be a reasonable indication that below 30°C and for very low conversion the chain transfer to polymer could be neglected in the radical polymerization of n-butyl acrylate. Supporting this assumption, it was very recently shown by Roos and Müller19) that, in the case of poly(n-BA) prepared by ATRP at 80°C, the α parameter decreases rapidly for high conversions (α = 0.67 for 50% conv. and 0.62 for 95% conv.) indicating long chain branching.

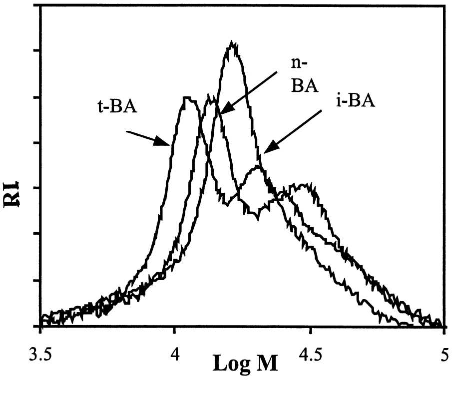


Fig. 6: MMD of n-butyl, i-butyl and t-butyl acrylates at -10°C in toluene solution. Runs of 300 to 600 pulses, 15 to 30 mJ/pulse, 100 Hz.

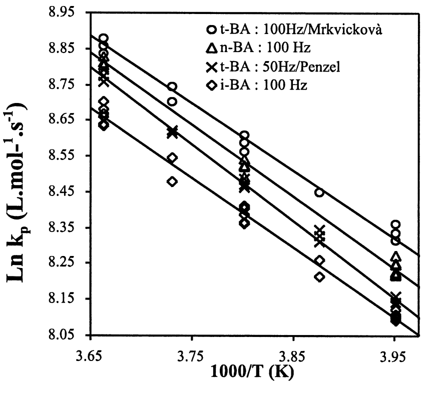


Fig. 7: Arrhenius plots from PLP of n-, i- and t-butyl acrylates in toluene solution. For t-BA the names correspond to the MHS parameters used (see text).

Considering our 100 Hz data in toluene (243 < T< 273 K), the linear regression of the Arrhenius plot led to,

$$k_{p,n\text{-}BA} = 10^{7.01}\ L\cdot mol^{-1}\cdot s^{-1}\cdot \exp\left(-\frac{16.61\ kJ\cdot mol^{-1}}{R\cdot T}\right) \text{ and } k_{p,n\text{-}BA}(20°C) = 11000\ L\ mol^{-1}\ s^{-1}$$

which correctly fits with the combined results obtained either in THF and toluene solutions or in bulk by Lyons et al[8) and Beuermann et al[9) from 208 to 303 K ($A_p = 10^{7.25}$ L mol^{-1} s^{-1}; E_a = 17.4 kJ mol^{-1}).

For i-butyl acrylate, we used the only available MHS values of Penzel and Goetz obtained from radical polymerization (K = 12.7 10^{-5} dL g^{-1}; α = 0.71)14), which for our data (100 Hz; $253 < T < 273$ K) led to,

$$k_{p,i\text{-}BA} = 10^{6.84}\ L\cdot mol^{-1}\cdot s^{-1}\cdot \exp\left(-\frac{16.08\ kJ\cdot mol^{-1}}{R\cdot T}\right) \text{ and } k_{p,i\text{-}BA}(20°C) = 9400\ L\ mol^{-1}\ s^{-1}$$

In the case of t-butyl acrylate and for experiments performed at 100 Hz, we used the values reported by Mrkvicková and Danhelka (K = 3.33 10^{-5} dL g^{-1}; α = 0.80)17). This α value has been recently confirmed for linear poly t-butyl acrylates18) and would remain valid as far as the long chain branching is negligible. Although it might be questionable in radical polymerization, in the above case of the polymerization of n-butyl monomer the transfer to polymer appears limited for low conversion, high frequency and low temperature PLP experiments, and thus we considered this should also apply for i-butyl and t-butyl acrylates. Working at 100 Hz in the range $243 < T < 273$ K, we obtained for t-butyl acrylate,

$$k_{p,t\text{-}BA} = 10^{6.84}\ L\cdot mol^{-1}\cdot s^{-1}\cdot \exp\left(-\frac{15.60\ kJ\cdot mol^{-1}}{R\cdot T}\right) \text{ and } k_{p,t\text{-}BA}(20°C) = 11300\ L\ mol^{-1}\ s^{-1}$$

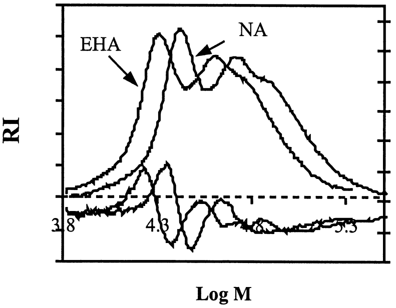
Surprisingly, experiments at 50 Hz led to much different values of k_p, suggesting the occurrence of long chain branching. Thus, we retreated the 50 Hz data using the parameters of Penzel and Goetz (K = 43.4 10^{-5} dL g^{-1}; α = 0.60)14) obtained from radical polymerization of t-butyl acrylate at 50-70°C and, owing to the low value of α, presumably long chain branched. The new values of k_p ($A_p = 10^{7.20}$ L mol^{-1} s^{-1}; E_a = 17.74 kJ mol^{-1}; k_p(20°C) = 11000 L mol^{-1} s^{-1}) obtained at 50 Hz appeared close to the ones determined at 100 Hz using the MHS parameters for linear polymer. Such a result supports that the assumptions made concerning the structure of the polymers were sound.

2-Ethylhexyl and Nonyl Acrylates

In the case of 2-ethylhexyl acrylate, the MHS parameters reported in literature are also strongly dependent on the type of polymerization and thus on the branching. The α exponent varies from 0.8 for linear samples prepared anionically (Schmitt16), Mrkvickova et al20)) to

0.68 for polymers prepared via radical polymerization at 50-70°C (Penzel and Goetz[14)]). Measurements performed on samples prepared in PLP conditions (5<T(°C)<25; bulk; very low conversions; 100 Hz) by Beuermann et al[9)] led to $\alpha = 0.695$. This indicates that even in the latter conditions long chain branching occurs significantly. Our PLP experiments (100 Hz; 42 runs of 100 to 600 pulses; 8 to 40 mJ/pulse) were performed from -25 to +10°C in toluene solution ($[M_o] = 2.5$ mol L^{-1}). Conversions were most generally comprised between 0.6 and 2.5 %. The data (Fig. 8-9) was treated using the MHS parameters of Beuermann ($K = 8.2\ 10^{-5}$ dL g^{-1}; $\alpha = 0.695$) as our conditions were close, and the linear regression led to:

$$k_{p,EHA} = 10^{7.23}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(-\frac{17.93\ kJ \cdot mol^{-1}}{R \cdot T}\right) \qquad 248 < T < 283\ K$$



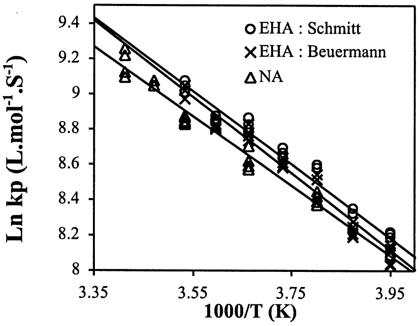


Fig. 8: MMD of 2-ethylhexyl and nonyl acrylates at -10°C in toluene solution. Runs of 100 to 900 pulses at 100 Hz.

Fig. 9: Arrhenius plots from PLP of 2-ethylhexyl and nonyl acrylates in toluene solution. MHS parameters from Beuermann and Schmitt (see text).

The calculated value of $k_p = 10700$ L mol^{-1} s^{-1} in toluene solution at 20°C is noticeably lower than the one obtained in bulk by Beuermann et al[9)] ($k_p = 16600$ L mol^{-1} s^{-1}). We added in Fig. 9 the Arrhenius plot obtained when treating our data with the MHS parameters for linear polymers (Schmitt[16)]), which led to $A_p = 10^{7.12}$ L mol^{-1} s^{-1}, $E_a = 17.25$ kJ mol^{-1} and $k_p(20°C) = 10900$ L mol^{-1} s^{-1}, values which are very close to the above ones. It should be also noticed that experiments performed at 50 Hz in the lowest temperature range (-25 to -15 °C) led to similar k_p values as at 100 Hz. Surprinsingly, for t-butyl acrylate, the variation of k_p due to the influence of possible long chain branching on MM determination appears negligible with respect to the decrease of k_p related to the apparent solvent effect.

In the case of nonyl acrylate, MHS parameters are not available yet and we used for calibration the MHS parameters measured by Beuermann et al$^{9)}$ for dodecyl acrylate, considering that chain flexibility, polymer-THF interaction parameter and extent of long chain branching might be comparable. This obviously gives only a rough approximation of the k_p and activation parameters:

$$k_{p,EHA} = 10^{6.88}\ L \cdot mol^{-1} \cdot s^{-1} \cdot \exp\left(-\frac{16.33\ kJ \cdot mol^{-1}}{R \cdot T}\right) \quad \text{and} \quad k_{p,NA}(20°C) = 9300\ \text{L mol}^{-1}\ \text{s}^{-1}$$

Conclusions

We examined (or reexamined) in this paper the PLP determination in toluene solution of the propagation kinetic parameters of a series of acrylates with increasing size of the alkyl side group. The results presented here are still preliminary but several conclusions can be drawn :

- depending on the nature of the acrylate and on PLP conditions (temperature, frequency, monomer concentration, conversion, etc..), transfer to polymer, and thus long chain branching, can critically interfere. The choice of the Mark-Houwink-Sakurada parameters is tricky as it is not possible to anticipate to wich extent branching will occur in a given PLP experiment , and the TD-SEC direct determination of these parameters on the medium of every experiment appears as the most confident technique.
- transfer to monomer and to toluene did not occur significantly in our PLP conditions and our temperature range since no broadening of MMD was observed, allowing generally to work with two inflection points.
- even if the data for i-butyl and nonyl acrylates need obviously to be confirmed, the k_ps measured in toluene solution present a tendency to continuously decrease when increasing the size of the side group (Fig. 10). This observation is conflicting with the reported behaviour for PLP experiments in bulk, revealing a possible solvent effect.

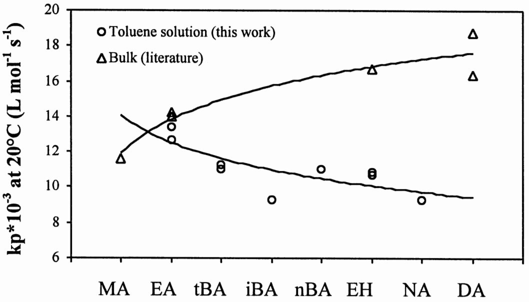


Fig. 10: Variations of the k_ps at 20°C, measured either in bulk (literature) or in toluene solution (this work), with the size of the side group for different alkyl acrylates.

Considering these conclusions, we are presently reinvestigating in more detail the behaviour of this series of acrylates, and we hope that we could soon contribute to the discussions of the IUPAC Group.

Acknowledgements

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References

1. O.F. Olaj, I. Bitai, G. Gleixner, *Makromol. Chem.* **186**, 2569 (1985) (and following papers)
2. M. Buback, R.G. Gilbert, R.A. Hutchinson, B. Klumperman, F.D. Kutcha, B. Manders, K.F. O'Driscoll, G.T. Russel, J. Schweer, *Macromol. Chem. Phys.*, **196**, 3267 (1995)
3. S. Beuermann, M. Buback, T.P. Davis, R.G. Gilbert, R.A. Hutchinson, O.F. Olaj, G.T. Russel, J. Schweer, A.M. Van Herk, *Macromol. Chem. Phys.*, **197**, 198 (1997)
4. R.A. Hutchinson, S. Beuermann, D.A. Paquet Jr, J.H. McMinn, *Macromolecules,* **30**, 3490 (1997)
5. M. Buback, B. Degener, *Makromol. Chem.* **194**, 2875 (1993)
6. L.G. Manders, *PhD Thesis*, T.U. Eindhoven (1997)
7. J.B.L. de Kock, *PhD Thesis*, T.U. Eindhoven (1999)

8. R.A. Lyons, J. Hutovic, M.C. Piton, D.I. Christie, P.A. Clay, B. Manders, S.H. Kable, R.G. Gilbert, *Macromolecules,* **29**, 1918 (1996)
9. S. Beuermann, D.A. Paquet Jr, J.H. McMinn, R.A. Hutchinson, *Macromolecules,* **29**, 4206 (1997)
10. S. Beuermann, M. Buback, C. Schmaltz, *Macromolecules,* **31**, 8069 (1998)
11. M. Buback, C.H. Kurz, C. Schmaltz, *Macromol. Chem. Phys.*, **199**, 1721 (1998)
12. O.F. Olaj, I. Bitai, F. Hinkelmann, *Makromol . Chem.* **188**, 1689 (1987)
13. J. Timmermans, in *Physico-chemical Constants of Pure Organic Compounds (IUPAC)*, vol. I, p. 153 and vol. II, p. 100, Elsevier, 1950
14. E. Penzel, N. Goetz, *Angew. Makromol. Chem.*, **178**, 191 (1990)
15. R.A. Hutchinson, D.A. Paquet Jr, J.H. McMinn, S. Beuermann, R.E. Fuller, C.Jackson, *DECHEMA Monogr.*, **131**, 467 (1995)
16. B. Schmitt, *Dissertation*, Johannes Gutenberg-Universität Mainz, April 1999
17. L. Mrkvicková, J. Dañhelka, *J. Appl. Polym. Sci.*, **41**, 1929 (1990)
18. G. Cheng, P.F.W. Simon, M. Hartenstein, A.H.E. Müller, *Macromol. Rapid Commun.*, **21**, 846 (2000)
19. G. Roos, A.H.E. Müller, *Macromol ; Rapid Commun.*, **21**, 864 (2000)
20. L. Mrkvicková, J. Dañhelka, P. Vlcek, *Polymer Commun.*, **31**, 416 (1990)