Effect of side chain branching on the structural and dynamic properties of linear and cyclic polyacrylates

Z. Benková[1*], T. Hrivnák[1,2]

[1]*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia*
[2]*IT4Innovations, VSB − Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava Poruba, Czech Republic*
[*]*zuzana.benkova@savba.sk*

Polyacrylates are extensively employed across various applications owing to their remarkable physico-chemical characteristics and the ease with which their properties can be taylored through modifications of the alkyl group in the alkoxycarbonyl substituent at relatively low cost.[1] Typically, this modification involves the linear extension of the alkyl group, which leads to monotonous trends in the structural and dynamic properties of polyacrylates in their melts.[2,3] Nevertheless, the impact of branching in the alkyl group on these properties remains inadequately explored and understood. This atomistic molecular dynamics study examines the structural and dynamic characteristics of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(isopropyl acrylate) (PiPA), poly(*tert*-butyl acrylate) (PtBA), and poly(methyl methacrylate) (PMMA) under different thermal conditions. The study considers both linear and cyclic polymer architectures. The distinction in architecture are detectable in the intermolecular radial distribution functions of Cα-Cα pairs. In the case of cyclic architecture, the radius of gyration and end-to-end distance of the polymer chains monotonously increase with the size of the alkyl group, whereas the polymer chain with linear architecture exhibit a non-monotonic trend in these quantities. This non-monotonous behavior for linear structures is explained by the competing effects of increased intrachain repulsion and diminished mutual penetration of the chain's pervaded volume as the alkyl group expands. The diffusion coefficient reflects an identical trend across the examined series for both architectures, with its non-monotonous behavior arising from the combined influence of the overall shape of the polymer chains and the symmetry of the alkyl group. Local dynamics are characterized by parameters related to α-relaxation and β-relaxation. Notable similarities in dynamic properties are observed between PEA and PiPA, as well as between PMA and PtBA, with the latter exhibiting slower dynamics. The slowest dynamics are recorded for PMMA.

Keywords: polyacrylates, molecular dynamics, diffusion, relaxation time, radius of gyration, radial distribution function, viscosity

Acknowledgments
This work was supported by grants APVV-21-0346, VEGA 2/0098/23, and SK-AT-20-0011.

References

[1] Cvek, M.; Kollar, J.; Mrlik, M.; Masar, M.; Suly, P.; Urbanek, M.; Mosnacek, J. Surface-Initiated Mechano-ATRP as a Convenient Tool for Tuning of Bidisperse Magnetorheological Suspensions toward Extreme Kinetic Stability. *Polym. Chem.* **2021**, *12*, 5093–5105.
[2] Kikuchi, H.; Tokumitsu, H.; Seki, K. Molecular Motions of Poly(ethyl acrylate) and Poly(*n*-butyl acrylate) Studied by Solid-State NMR and Molecular Dynamics Computer Experiments. *Macromolecules* **1993**, *26*, 7326–7332.
[3] He, X.; Wu, J.; Huang, G.; Wang, X. Effect of Alkyl Side Chain Length on Relaxation Behaviors in Poly(*n*- alkyl Acrylates) and Poly(*n*-alkyl Methacrylates), *J. Macromol. Sci. Phys. B* **2011**, *50*, 188–200.