

Polymer and Colloid Highlights

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Homo- and Copolymers of Cationic Double-Charged Monomers

Ricardo Losada, Hamideh Ahmadloo, and Christine Wandrey*

*Correspondence: PD Dr. C. Wandrey, Institute for Bioengineering and Institute for Chemical Sciences and Engineering, EPF Lausanne, Station 15, CH-1015 Lausanne, Tel. +41 21 693 96 61, Fax: +41 21 693 96 85, E-Mail: christine.wandrey@epfl.ch

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Water-soluble synthetic polyelectrolytes (PEL) have found many practical applications, which usually rely on strong electrostatic interactions in solution or at interfaces. The majority of new water-soluble PEL structures were obtained by polymer modification or copolymerization. Relatively few have been synthesized by polymerizing new monomers. Recently, two cationic double-charged monomers became available; 1,3-bis(*N,N,N*-trimethylammonium)-2-propylmethacrylate dichloride (di-M) and 1,3-bis(*N,N,N*-trimethylammonium)-2-propylacrylate dichloride (di-A) (Fig. 1).^[1] So far, synthetic monomers have been limited to structures which yield PEL with a maximum of one charge per 0.25 nm monomer unit length. The PEL from the new monomers have the twofold charge density, which is in the range of biomacromolecules such as DNA.

These monomers provided the opportunity to study polymerization processes under strong electrostatic influence, to verify theoretical predictions concerning the solution behavior of highly

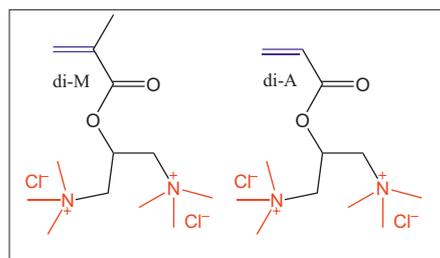


Fig. 1. Chemical structures of the cationic double-charged monomers di-M and di-A.

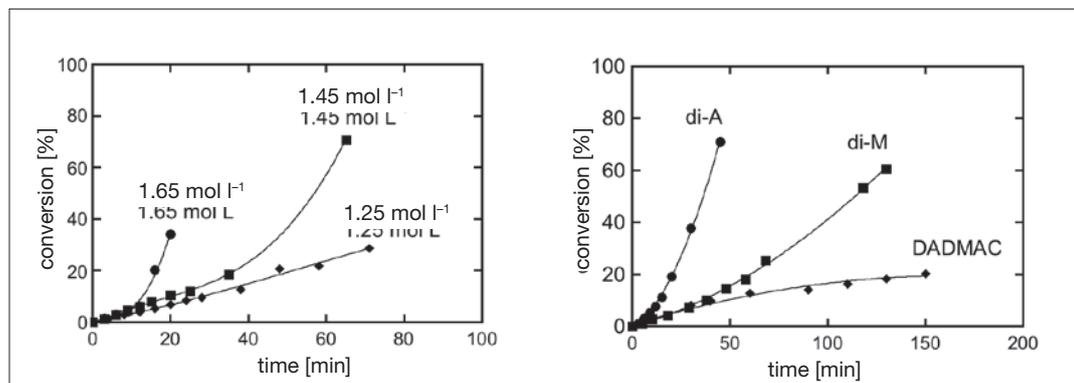


Fig. 2. Auto-acceleration. Left: for different di-M concentrations, right: at $1.25 \text{ mol} \times \text{l}^{-1}$ for different monomers. For the less charged diallyldimethylammonium chloride (DADMAC), auto-acceleration was even not observed at $4 \text{ mol} \times \text{l}^{-1}$.

charged flexible PEL, and to synthesize and test novel homo- and copolymers.

For di-M and di-A, monomer reaction orders of 4.4 and 3.9 were determined.^[2] Such high orders have not yet been reported for any other monomer. Another phenomenon is the auto-acceleration of the radical polymerization which already starts at conversions of less than 10% and at relatively low monomer concentration (Fig. 2).^[2] Increasing the ionic strength shifted the onset of the auto-acceleration to higher conversion, thus confirming electrostatic interactions as the origin of this phenomenon.

The free radical copolymerization of di-M with its mono-charged counterpart and with other cationic and neutral monomers allowed the influence of the charge density and the charge location on the monomer reactivity to be assessed. The dominating influence of the location of the growing radical relative to the charges was clearly demonstrated.^[3]

For the homopolymers, counterion activity coefficients of 0.11 confirmed the theoretical prediction.^[2] For copolymers with acrylamide, deviation from the theoretical counterion activity suggests the impact of the charge distribution.^[3]

The methyl group adjacent to the double bond not only influences the polymerization behavior but also the physical properties of the polymers. Whereas poly-di-M was stable at pH = 9, hydrolysis of poly-di-A occurred already at pH = 7.4.

The homo- and copolymers of di-M and di-A and derivatives are interesting for a number of applications where high charge density is requested. Replacing the chloride in the monomers by dicyanamide and performing the polymerization in dicyanamide ionic liquids yielded polymeric ionic liquids with interesting properties.^[4]

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If you are interested in submitting a new highlight, please contact:

Prof. Michal Borkovec, University of Geneva,
E-mail: michal.borkovec@unige.ch, Tel.: +41 22 379 6053