

Relaxation methods for studying transformations in polymer systems

K. L. Levine^{✉1}, J. O. Iroh², D. E. Tallman³

¹ Telecommunication Academy named after S. M. Budyonny, 3 Tikhoretsky Ave., Saint Petersburg 194064, Russia

² University of Cincinnati, 2600 Clifton Ave., Cincinnati OH 45221, USA

³ North Dakota State University, 1340 Administration Ave., Fargo ND 58105, USA

Authors

Kirill L. Levine, e-mail: levinkl@hotmail.com, ORCID: [0000-0002-1050-6609](https://orcid.org/0000-0002-1050-6609)

Jude O. Iroh, ORCID: [0000-0003-0778-4023](https://orcid.org/0000-0003-0778-4023)

Dennis E. Tallman

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Abstract. It is known that self-organisation of nanostructures according to the bottom-up approach is driven by the competition of several processes: surface tension, diffusion, gravity, buoyant force and, perhaps, molecular coordination phenomenon. The last one was discussed in the 70s in terms of the so-called “mobile organised molecular arrays” and proved with the help of nuclear magnetic relaxation. This study shows examples of self-organised structures obtained electrochemically by authors and provides a discussion regarding the same terms.

Keywords: self-organisation, nuclear magnetic relaxation, polymers, relaxation processes, microcontainers.

Introduction

One of the most important ecological problems of the 21st century is plastic pollution. Using self-disposable (biodegradable and self-degradable) polymer containers can be a solution; therefore, creating smart recycling polymers is a matter of high priority. It is important to understand processes underlying polymerisation in order to create polymers with “smart” behaviour. One of such processes is self-organisation, which is taking place during polymerisation or cooling of the polymer melt.

Self-organisation resulting in growth of nanostructures is considered to be an example of the bottom-up approach as described in (Faynman 1960). Later ideologists of nanotechnology (Lehn 1988; Nicolis, Prigogine 1977) described self-organisation as competition between several forces: surface tension, diffusion, buoyant force, gravity and phenomena related to coordination, for example, atoms of transition elements and catalysis. These factors are responsible for the variety of forms appearing during polymerisation. Self-organisation in polymers occurs not only due to polymerisation of monomers but also due to the cooling of polymer and oligomer melts below glass transition temperature (T_g). It results in the appearance of peculiar formations, such as spherulites, lamellae and folds. It is believed that polymers demonstrate a specific mechanism of self-organisation that utilises the so-called “mobile organised molecular arrays” or “labile pre-pregs” (LP) (literal translation from Russian)—aggregation of monomers in the condition of chaotic movement (Gvozdetskii et al. 1968). Those arrays are capable of moving along the sample and responsible for morphological significances.

Relaxation methods

Fundamentals of relaxation processes in liquid dielectrics and melts are based on hydrodynamic (Debye 1929) and kinetic (Frenkel 1946) models. A modification for these models was made by Fröhlich (1958) and Davidson et Cole (1951). The most recognised equations for dielectric relaxation are the Cole–Cole (Cole, Cole 1941), the Havriliak–Negami (Havriliak, Negami 1967) and the Fuoss–Kirkwood (Fuoss, Kirkwood 1941) equations.

Viscous polymer systems differ both from the Cole–Cole and from the Fuoss–Kirkwood models, so modifications have to be made to them.

It should be noted that two relaxation methods—dielectric spectroscopy and nuclear magnetic relaxation (NMR relaxation)—are widely used for studying molecular order and mobility in polymer systems. For example, both of them are used in (Borisova et al. 1980). However, due to the specific organisation of scientific experiments, the present research is based on the NMR relaxation as the majority of results relevant to this paper were obtained by this method.

Nuclear magnetic relaxation

The majority of studies on relaxation processes in dielectric melts were carried out by NMR relaxation methods. Theoretical background developed by Bloembergen, Purcell, and Pound (Bloembergen et al. 1948) describes relaxation phenomena caused by dipole–dipole interactions of atomic nuclei. The system of nuclear spins forms a thermodynamic spin subsystem. The local magnetic field of this subsystem is sensitive to atomic environment. It can be studied by external alternating magnetic field.

Nuclear magnetic relaxation study: Oligoetheracrilates

NMR relaxation is widely used for studying various polymers and polymer systems (Besghini et al. 2019), such as polystyrene (Gasilova et al. 1993), micellar and liquid crystalline systems (Wong 2006), polyhydroxyalkanoates (Nishida et al. 2018), polyfluoroacrylates (Borisova et al. 1980) and especially tetrafunctional oligoetheracrilates (OEA) (Fig. 1). The characteristic OEA feature is the formation of insoluble three-dimensional oligomers at early stages of their polymerisation. To explain this phenomenon, Gvozdetskii, Azizov, Gorbunova et al. (Gvozdetskii et al. 1968) suggested that molecules in liquid monomer and polymer systems with acrylic end-groups are set in ordered kinetically preferred states. Those states (LP) were essentially studied by Berlin's group.

Several (from 3 to 5) relaxation areas are characteristic of molecular mobility processes: α , β , and γ transitions (in some cases additional β' ; γ' relaxations are present) (Berlin et al. 1983). Local relaxation processes related to small-scale movements of side groups and main network chains are referred to as β and γ transitions. They occur at lower temperatures, typically 140–180 K.

β' -type relaxation is observed due to freezing of mobility in complex oligomeric chains; for instance, in oligomeric chains containing complex ether groups. Rotational isomerism and rotational vibrations are sometimes believed to be primarily responsible for this type of relaxation.

Additional γ' relaxation is observed in the case of side methane groups are present in some OEAs, e.g. oligocarbonmethacrylate. Rotation of these groups occurs at higher temperatures.

Processes of a relatively larger scale involve the motion of molecular chain parts with side groups and side chains; oligomers attached to them are known as α relaxation, glass transition being an example (230–360 K).

In three-dimensional (spatially linked) polymers, relaxation processes tend to unite and become non-recognisable (Berlin et al. 1966), which, in turn, can be a sign of a complicated self-assembling process through an intermediate LP stage. Formation of lamellae, globules, and other morphological species suggests the influence of long-range interactions on their creation. Indeed, in α , ω -bis / methacryloiloxy ethyleneoxy carbonyloxy/-1,3-propylene (MEKP) ($R = -(\text{CH}_2-\text{CH}_2-\text{CH}_2)-$) the average size of globules was 1 μm (Table 1), which exceeded the definition of “nano”. In three-dimensional polymers, such as phenol formaldehyde (Spurr et al. 1957) and epoxy resins (Basin et al. 1972; Erath, Spurr 1959), polymaleinates (Spurr et al. 1957) existence of non-uniform morphology was shown at microscopic scale. For example, for α and γ MEKE ($R = -(\text{CH}_2-\text{CH}_2)-$ (α , γ -bis / methacryloiloxy ethyleneoxy carbonyloxy/-1,3-ethylene) aggregation of primary globules followed by the formation

of anizodiametric structures with a characteristic size of 600–800 Å was observed, which was confirmed by SEM and SAX data.

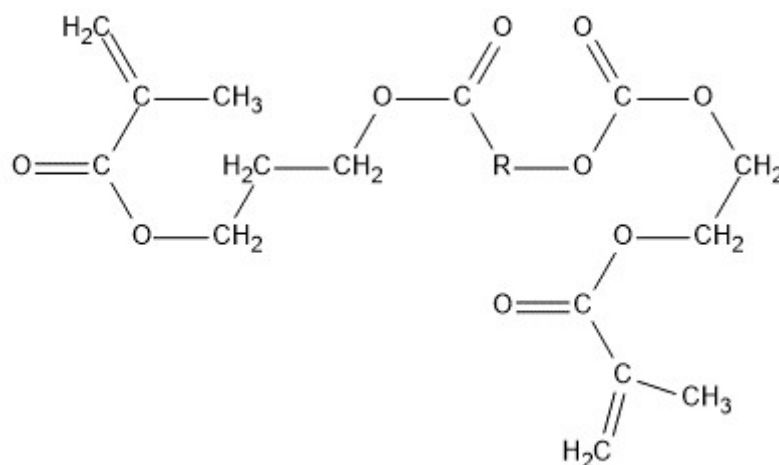


Fig. 1. Tetrafunctional oligoetheracrylates

Supramolecular structure arising during polymerisation in complex polymers (terminology as cited in the original) was discussed by Berlin, Kireeva and Sivergin (1974). Their research concluded that the supramolecular organisation of polymers with highly ordered links of concentration higher than $5 \cdot 10^{20} \text{ cm}^{-3}$ attained non-uniform, globular structure. The examples of such polymers are phenol-formaldehyde and epoxy resins, polymaleinates, diallyl terephthalates.

Other researchers (Berlin 1970; Berlin et al. 1974; Berlin et al. 1983) came to the same conclusions, stating that the formation of stacked and liquid-crystalline structures was possible in the case of alternating chemically active groups in the structurally regular liquid OAE oligomers. The stability of supramolecular structures was defined by the time of structural relaxation, which, in turn, depends on molecular spatial packing density, magnitude of intermolecular relaxation, viscosity, external conditions, dimensions of pre-cursor oligomers, and polymerisation conditions. Polymerisation conditions stand for the comprehensive influence of operating parameters (vibration, stirring, electromagnetic fields), physical conditions (temperature and pressure), as well as purity and homogeneity of oligomer mixture and other wide range of factors influencing the supramolecular polymer structure. Self-organisation with LP participation is believed to be of interest both for academic and applied science.

In polymers below T_c the scale of pre-pregs containing micelles in sterically preferable positions by the order of magnitude can become close to micelles, distinguishable by electronic microscopy.

Table 1. Average globule size for some OEAs

R	Title	Acronym	Globules size, A
R1	methacryloiloxy ethyleneoxy carbonyloxy/-1,3-ethylene	MEKE	600–800
R2	methacryloiloxy ethyleneoxy carbonyloxy/-1,3-propylene	MEKP	200–1000
R3	methacryloiloxy ethyleneoxy carbonyloxy/-1,3-dimethyl propylene	MEKNPG	1000–1500

Above T_c relaxation studies revealed the existence of complex two-componential absorption lines in OAE, which are defined by Strzlecki, Liebert (1973) as a “molecular collective” formed by Van der Waals (for non-polar) and dipole-dipole (for polar) molecules. Moreover, it was revealed that molecules in LP exist in the condition of continuous movement and re-organisation, in contrast to relatively stable lamellae above T_c . However, it is not surprising, considering lowered steric limitations at temperatures $T \geq T_c$, but close to T_c , exactly up to $T_c + 40^\circ$. Above the established upper limit, the lifetime of molecular associates became exclusively small ($<10^{-4} - 10^{-5} \text{ s}$).

In the course of conducted experiments various polymer structures were obtained electrochemically. Electrochemical deposition of conducting polymers onto metal surfaces was performed primarily for the purpose of corrosion protection (Iroh et al. 2003). Examples of morphologies, obtained electro-

chemically, are shown in (Fig. 2) (Levine et al. 2005; 2019). Different electrolyte composition and formation surface resulted in dendritic (Fig. 2A) and vase-looking (Fig. 2B, C) morphologies, which possibly involved air bubbles driven by buoyant force. A structure typical to polypyrrole cauliflower (Fig. 2D) served as a surface for the formation of inverse bell (Fig. 2E), bell (Fig. 2F) and egg-looking (Fig. 2G) morphologies; morphologies obtained by others researches, demonstrated similar bell-shape PPy structures (Ammam 2012), and rectangular patterns (Sapurina, Shishov 2012).

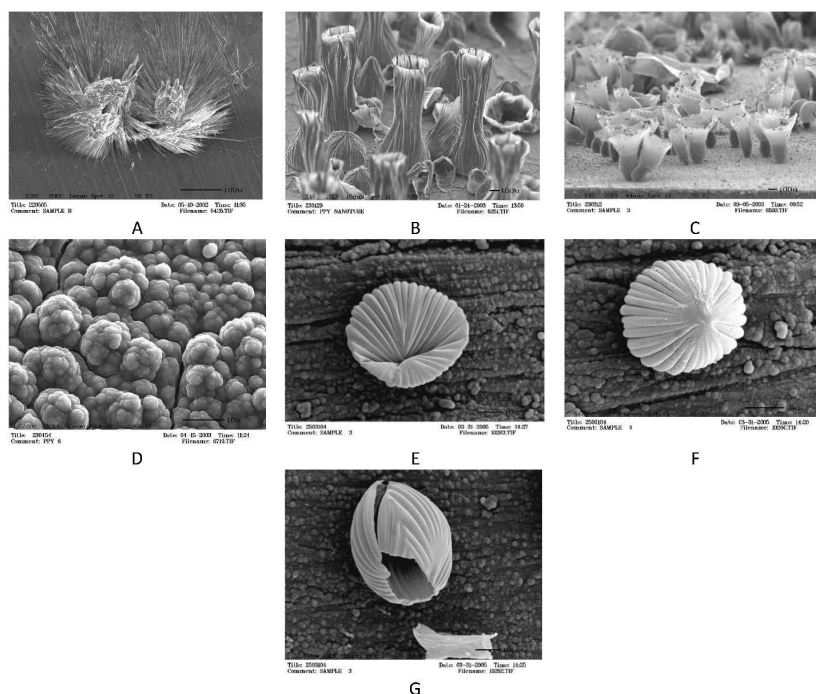


Fig. 2. Morphologies obtained electrochemically

Conclusion

Self-assembling occurs in the process of chemical and electrochemical polymerisation of polymers. As a result, complicated morphologies are formed according to the bottom-up approach. These morphologies belong to both nano and micro-scales. Examples of these morphologies are globules, micelles, lamellae, folds, and microcontainers. Relaxation methods, in particular, nuclear magnetic relaxation and dielectric spectroscopy are sensitive to general parameters related to self-assembling, being together with microscopic methods, a way of its visualization.

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