

# Three-Dimensional Free-Radical Polymerization

Gennady V. Korolev · Michael M. Mogilevich

# Three-Dimensional Free-Radical Polymerization

Cross-Linked and Hyper-Branched Polymers

 Springer

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# Preface

At present, three-dimensional free-radical polymerization (TFRP) is a special field of radical polymerization. TFRP is characterized by specific kinetic regularities and mechanisms of processes for the formation of cross-linked or hyper-branched polymers, and they are different from the kinetics and mechanism of classical radical polymerization.

The fundamental studies of kinetics and mechanism of TFRP with formation of cross-linked polymers have been carried out in three stages. The first stage lasted from 1960 until 1983, and the main mechanisms of TFRP of oligo(acrylates) were established during this stage [1–3]. Condensation telomerization, being a universal oligo(acrylate) synthesis procedure, allows us to vary certain molecular parameters, such as length and flexibility of oligomeric blocks, number and type of reactive groups (methacrylic or acrylic groups), and chemical nature of atomic groups of an oligomeric block, which represent the centers of strong intermolecular interactions. For this reason, oligo(acrylates) were very convenient compounds for establishing the main kinetic regularities of TFRP and regularities of formation of polymer three-dimensional cross-linked structures, according to the so-called microheterogeneous mechanism (G.V. Korolev, 1977), at the topological and morphological levels. During the second stage, which lasted from 1983 until 1995, the kinetic regularities of TFRP were studied in depth, and additional evidentiary data in favor of the microheterogeneous mechanism of TFRP were found [4, 5]. The last, or third stage (from 1995 until 2005) involved exploration of TFRP under the “living” chains conditions and identification of new regularities associated with the implementation of these conditions [6], as well as the creation of the new gelation theory applicable to TFRP, investigation into physical and mechanical properties of cross-linked copolymers, and the interpretation of these properties within the framework of the physical network model [6].

The technical value of TFRP is generally known. Industrial use of oligo(acrylates), oligo(estermaleates) in styrene compositions, and oligo-esters modified by fatty acids of vegetable oils (alkyds) is based on TFRP with cross-linked polymer formation. The interest in TFRP throughout the world has markedly increased in the 1990s: by 2000 the number of publications on TFRP had grown tenfold. This growth is explained by the development needs of microelectronics, fiberoptics, and data storage and transmission devices. TFRP makes polymers highly attractive for

applications related to high-tech materials. The radical chain nature of TFRP enables performing curing of fluid polyunsaturated methacrylates in superfast time (seconds!) and an easily controlled mode at normal temperature.

It was found, in the middle of the 1990s, that in addition to cross-linked polymers TFRP can also lead to the formation of hyper-branched polymers (HBP) (non-cross-linked) that have a unique chemical structure and properties which are different from the structure and properties of all known linear and cross-linked polymers. Polymer chains of HBP diverge outward symmetrically in three-dimensional space from the point or linear center of symmetry and look like a branching tree. The unique properties of HBP turned out to be so popular that during the next decade these polymers found use in various applications for polymer materials from microelectronics to medicine. They caused a revolution in polymer materials technology. And, all this gave a new powerful impulse to the development of the entire TFRP field—the intensive and successful investigation into cross-linked polymers synthesized by TFRP conducted for many years did not betoken such a “burst” of interest. Judging by the trends in publications on this issue, this new subfield has developed extremely fast: before 1997, only a few publications appeared per year, during 1997–1998 the number of publications increased to 100, and during 2000–2005 more than 250 articles and patents per year have appeared.

The first part of this book deals with TFRP with formation of cross-linked polymers. It is based mainly on the results of systematic research of the authors and their colleagues.

This part (Chapters 1 through 6) includes all available data (plus analysis of these data) indicating the microheterogeneous character of TFRP. The microheterogeneous mechanism of TFRP includes both polymerization specifics at the initial, intermediate, and final stages (namely, initial formation, growth, and merger of polymer grains performing the function of autonomous micro-reactors) and structural and physical transformations in the course of TFRP (micro-syneresis, microredistribution, and local glass transition).

The interpretation of the main kinetic regularities of polyunsaturated oligomer polymerization in blocks and solutions and kinetic specifics of inhibited TFRP is given taking into account the microheterogeneous mechanism of TFRP. The main regularities of the polymerization of polyunsaturated compounds of vinyl and allyl types in a film under the conditions of oxygen diffusion were explained in the context of the proposed layer-by-layer TFRP model. A model of regular kinetically active associates intended for interpreting kinetic abnormalities of oligo(acrylates) and alkyl methacrylates polymerization is proposed: this model is substantiated both kinetically and via computer simulation. Basic kinetic features of the three-dimensional copolymerization of polyunsaturated (cross-linked) oligomers and monounsaturated (non-cross-linked) vinyl monomers were identified.

The main issues of the new branch in free-radical polymerization—namely, “living” chain three-dimensional free-radical polymerization—are analyzed. Also, exhaustive description is given for all studies on TFRP in the “living” chain mode and the role of this mode for the macromolecular design of cross-linked polymers.

The new theory of gelation in the TFRP process, which was developed by V. I. Irzhak and G.V. Korolev in 2000–2003, is described in depth. This theory is

alternative to the well-known Flory–Stockmayer theory, which is unjustifiably applied to TFRP. Critical conversion (gel point) for various modes of free-radical polymerization is determined in numerical form, and the obtained results are generalized in formulas.

Physical, mechanical, and thermo-mechanical properties of cross-linked (poly) acrylates and cross-linked copolymers of oligomers with vinyl monomers are analyzed in the context of the physical network model (i.e., intermolecular interactions system approximated by network of physical links). The predominant role of the physical network (i.e., a network of physical junctions) in proposed mechanisms for the transition of cross-linked copolymers into high-elastic and forced-elastic states is revealed. Problems of macromolecular design of cross-linked polymers and copolymers are also discussed.

The second part of the book [Chapters 7, 8] is devoted to methods of synthesis, properties, and application of hyper-branched polymers (HBP). An extensive array of information (about 400 publications) is systematized and reviewed. A classification of synthesis methods for HBP, which is based on mechanisms of synthesis reactions, is proposed. Methods for HBP synthesis by three-dimensional free-radical polymerization (with regulation of polymeric chains length due to the variation of initiation rate, employment of chain transfer agents and chain transfer catalysts, and intrachain reactions of radical chain carriers) are discussed in detail with examples. A mathematical model of HBP synthesis by the TFRP method under the conditions of unlimited supply of oxygen is proposed, and results of prediction obtained through the use of this model are presented.

The most successful and representative options of HBP synthesis by “living” chain free-radical polymerization are reviewed in depth because it is in just this case that the topological structure of HBP is distinguished by the maximum degree of regularity, which makes the HBP topological structure similar to the structure of regular HBP dendromers. Also, the method of “living” TFRP makes it possible to synthesize HBP with a sophisticated structure of macromolecules (nanostructured polymers).

Large amounts of information on practical application of HBP are systematized in this book in the form of generalized tables for the sake of convenience for readers. Particular emphasis is placed on HBP that are already produced industrially and on methods for modifying them in the context of specific applications.

Analytical reference materials for the subject matter of this book are given in the Appendix (Chapter 9). A short description of experimental methods that proved to be effective for studying the TFRP kinetics and mechanism, as well as the structure and properties of cross-linked polymers, is also given in the Appendix.

Thus, the authors have tried to give an integral description of scientific and applied aspects of three-dimensional free-radical polymerization with formation of both cross-linked and hyper-branched polymers as well as to outline the current state and trends of the development of this specific area of free-radical polymerization. The readers are to judge whether the authors have succeeded.

*Chapters 1 and 2 were written by G.V. Korolev and M.M. Mogilevich, and Chapters 3, 4, 5, 6, 7, 8, and 9 were written by G.V. Korolev.*

St. Petersburg, July 2008

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To our deep sorrow one of the authors of the present book – Gennady Vladimirovich Korolev – passed away between its publication in Russian and in English. Therefore, publication of the English version, which was planned by him, is a tribute to the memory of the outstanding scientist he was and a solace for the members of his family and colleagues.

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# Abbreviations

|           |   |
|-----------|---|
| AcN       | Acetonitrile  |
| AIBN      | 2-2'-Azo-bis-isobutyronitrile   |
| ATRP      | Atom transfer radical polymerization  |
| BA        | Butyl acrylate  |
| BD        | Tetra(methylene glycol)   |
| BDOdMA    | Buthane diol dimethacrylate   |
| BMA       | Butyl(meth)acrylate   |
| BP        | Benzoyl peroxide  |
| BPh       | Benzophenone  |
| BQ        | 1,4-Benzoquinone  |
| CEA       | Cetyl acrylate  |
| CTA       | Chain transfer agent  |
| CTC       | Chain transfer catalysis  |
| dAl-EGA   | Diallyl ethylene glycol adipate   |
| DB        | Degree of branching   |
| DC        | <i>N,N</i> -Diethylamino-dithiocarbamates group                             |
| DCM       | Dichlormethane  |
| DCPD      | Dicyclohexyl peroxydicarbonate  |
| DDA       | Dodecyl acrylate  |
| DDMA      | Dodecyl methacrylate  |
| DDOdMA    | Dimethacrylate 1,10-decandiol   |
| dEG       | Di(ethylene glycol)   |
| dEGbMAOEC | Oligomers of diethylene glycol bis(methacryloyloxyethyl carbonate) or OCM-2 |
| DHHP      | Di(1-hydroxycyclohexyl) peroxide  |
| dMA       | Dimethacrylate  |
| dMABDO    | Dimethylacrylate-1,4-butandiole   |
| dMA-BGA   | Oligomers of dimethacrylate butylene adipate                                |
| dMA-BGPh  | Oligomers of dimethacrylate butane-1,4-di-ol phthalate, various MW          |
| dMA-BGSb  | Oligomers of dimethacrylate butylene glycol sebacate                        |
| dMA-dEGPh | Oligomers of dimethacrylate diethylene glycol phthalate                     |
| dMAEG     | Di(methacrylate) (ethylene glycol)  |

|           |   |
|-----------|---|
| dMA-EGA   | Oligomers of dimethacrylate bis(ethylene glycol) adipate  |
| dMA-EGPh  | Oligomers of dimethacrylate ethylene glycol phthalate   |
| dMA-EGSb  | Oligomers of dimethacrylate ethylene glycol sebacate  |
| dMAHDO    | Dimethylacrylate-1,6-hexandiol  |
| dMAPDO    | Dimethylacrylate-1,3-propandiol   |
| dMA-tEGPh | Oligomers of dimethacrylate bis-(triethylene glycol) phthalate  |
| DMFA      | Dimethyl formamide  |
| DMPA      | 2,2-Dimethoxy-2-phenylacetophenone  |
| DSC       | Differential scanning calorimetry   |
| DVB       | Divinyl benzene   |
| FES       | Forced-elastic state  |
| FM        | Foreign matter  |
| GPC       | Gel-permission chromatography   |
| HBP       | Hyper-branched polymer  |
| HDOdMA    | Dimethacrylate 1,6-hexanediol   |
| HEMA      | (2-Hydroxy)ethyl methacrylate   |
| hMA-PeA   | Oligomers of hexamethacrylate (bis-pentaerythritol) adipate   |
| HP        | Hydroperoxide   |
| IMI       | Intermolecular interactions   |
| IR        | Infrared spectroscopy   |
| LALLS     | Low angle laser light scattering  |
| LRP       | Living radical polymerization   |
| LS        | Light scattering  |
| MA        | Methyl acrylate   |
| MBP-(1-3) | Oligomers of dimethacrylate tetramethylene glycol phthalate, various MW, is used in Tables 2.1, 2.4, 2.5 only, dMA-BG |
| MDA       | Oligomers of dimethacrylate diethylene glycol adipate, various MW, is used in Tables 2.1, 2.4, 2.5 only               |
| MDP-(1-5) | dMA-dEGPh, is used in Tables 2.1, 2.4, 2.5 only   |
| MDS       | Oligomers of dimethacrylate diethylene glycol sebacate, various MW, is used in Tables 2.1, 2.4, 2.5 only              |
| MDU       | Oligomers of dimethacrylate diethylene glycol 5,5'-thiodivalerate, various MW, is used in Tables 2.1, 2.4, 2.5 only   |
| MEP       | dMA-EGPh, is used in Tables 2.1, 2.4, 2.5 only  |
| MHP       | dMA-BGA, is used in Tables 2.1, 2.4, 2.5 only   |
| MMA       | Methyl methacrylate   |
| $M_n$     | Number average molecular weight   |
| $M_w$     | Weight average molecular weight   |
| MWD       | Molecular weight distribution   |
| NMP       | Nitroxide-mediated radical polymerization   |
| NonA      | Nonyl acrylate  |

|           |   |
|-----------|---|
| NonMA     | Nonyl methacrylate  |
| OCA-4     | Oligomers of tetraethylene glycol bis(acryloyloxyethyl carbonate)     |
| OCA-6     | Oligomers of hexaethylene glycol bis(acryloyloxyethyl carbonate)      |
| OCM-2     | dEGbMAOEC   |
| OCM-4     | Oligomers tetraethylene glycol bis(methacryloyloxyethyl carbonate)    |
| OCM-6     | Oligomers hexaethylene glycol bis(methacryloyloxyethyl carbonate)     |
| PDB       | “Pendent” double bonds  |
| PDOdMA    | Propane diol dimethacrylate   |
| PMR       | <sup>1</sup> H-NMR  |
| polyEGdMA | Poly(ethylene glycol) dimethacrylate                                  |
| PS        | Poly(styrene)   |
| RAFT      | Reversible addition fragmentation chain transfer                      |
| RTIR      | Real-time infrared spectroscopy                                       |
| teAl-tPA  | Tetraallyl of (trimethylol propane adipate)                           |
| tEG       | Tri(ethylene) glycol  |
| tEGdMA    | Tri(ethylene glycol) dimethacrylate                                   |
| teMA-tEA  | Oligomers of tetra(meth)acrylate trimethylolethane adipate (teMA-tEA) |
| teMA-tPA  | Oligomers of tetra(meth)acrylate bis(trimethylolpropane) adipate      |
| TEMPO     | 2,2,6,6-Tetramethylpiperidiny-1-oxy                                   |
| TFH       | 2,4,6-Triphenyl-1-hexene  |
| TFRP      | Three-dimensional free-radical polymerization                         |
| THF       | Tetrahydrofuran   |
| TMTD      | Tetramethyl-thiuramdisulfide  |
| TNT       | 2,4,6-Trinitrotoluene   |
| TS        | Breaking tensile strength   |
| VA        | Vinyl acetate   |

**Part I**  
**Three-Dimensional Free-Radical  
Polymerization. Cross-Linked Polymers**

# Chapter 1

## Microheterogeneous Mechanism of Three-Dimensional Free-Radical Polymerization

**Abstract** For the first time, the microheterogeneous mechanism of three-dimensional free-radical polymerization, initially disclosed by the authors in Russian in a number of publications during a period from 1970 to 1995, is here consistently described in English and supported by sufficient proof. This process gives products having complex multilevel cross-linked structure, namely, highly cross-linked polymeric grains and low cross-linked intergrain layers; in their turn, grains of “core-shell” structure and interlayers are also nonuniform in terms of degree of cross-linking of the polymer network at different conversions.

The very concept of the microheterogeneous character of highly cross-linked polymer formation processes was rather precisely presented by Howink as early as in 1934 [1]. Further development of this idea is reflected in works written by Kozlov [2, 3], Gallacher and Bettelheim [4], Korolev and Berlin [5], Notley [6], Bobalek et al. [7], and Dušek [8]. Exploration into the generation and growth of microgel particles during polymerization of unsaturated oligo-esters [4], and the appearance of a hypothesis on the formation [during the polymerization of oligo(acrylates)] of discrete microgel particles, in which a local gel effect is developed [5], contributed to the substantiation of ideas related to the three-dimensional free-radical polymerization (TFRP) mechanism. A TFRP mechanism that includes microheterogeneity [9] was formulated in 1970 based on new experimental data. The phenomenon of microsineresis in the process of highly cross-linked macromolecular structure formation [8] was discovered in 1971. However, only studies that took many years and were focused on polymerization of model objects, with intentionally varied structure, plus exploration into the structure of formed polymers conducted with the use of specially developed methodologies, enabled researchers to obtain strict experimental proofs of the microheterogeneous TFRP mechanism [10]. Only then did the hypothesis turn into a proven concept, and now a TFRP model suitable for quantitative calculations has appeared.



## 1.1 Microheterogeneous Model of Polymerization Process

The essence of the model at the qualitative level consists of the following [10]. The radical polymerization of polyunsaturated compounds leads to formation of polymer coils even at low conversions (i.e., even at pre-gel state) as a result of inter- or intrachain aggregation of polymer chains containing “pendent” double bonds. The diffusion-limited rate of chain termination is decreased in such coils with increasing local viscosity and, as a consequence, the polymerization rate is increased, which, in its turn, leads to further growth of viscosity. Locally (in polymer coils), the polymerization process develops autocatalytically, as a result of which polymer coils turn into highly cross-linked polymer particles (grains). With an increase in the degree of primary macromolecules branching, the probability of intramolecular cross-linking (cyclization) increases, which promotes the formation of microgel particles (grains). The concentration of polymer grains in the reaction medium stops increasing even at the initial stage of conversion, and subsequent polymerization is effected via buildup of new layers of cross-linked polymer from the surface of the grains. Such grains play the role of self-contained micro-reactors, in the surface layers of which the polymerization process is localized. At later stages of polymerization, grains come into contact with one another (as a result of their growth), and the accretion of grains into a monolith in the zones of such contact takes place. The specific character of TFRP process lies in the fact that practically starting from low conversions, a homogeneous reaction system becomes a micro-nonhomogeneous system consisting of highly cross-linked polymer particles that are poorly interconnected with penetrating chains.

The polymerization, i.e., the chemical transformation proper, is accompanied by secondary physical processes, namely, aggregation of polymer chains, microsineresis with isolation of an initial oligomer from quite highly cross-linked micro-volumes of initial oligomer (with certain components dissolved in this initial oligomer—initiators, inhibitors, and other additives), and local glass transition of these highly cross-linked micro-volumes.

The micro-nonhomogeneous reaction medium (in terms of polymer network cross-linking degree) becomes microheterogeneous after the beginning of local glass transition. Also, TFRP and structural physical processes are mutually interconnected. The aggregation of polymer chains accelerates polymerization in cross-linked polymer coils, which, in turn, leads to the accelerated development of local syneresis (microsyneresis) and local glass transition within the coils. In the end, instead of a polymer with macromolecular network uniformly distributed within the volume, a polymer is formed that consists of highly cross-linked volumes (grains) separated by low cross-linked (defective) interlayers.

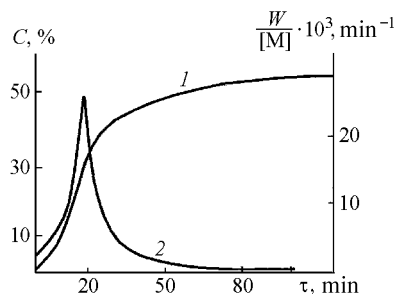
Thus, according to the microheterogeneous model, in the course of TFRP a set of kinetic, thermodynamic, and topological factors causes structural and physical transformations, which accompany the chemical reaction of polymerization and result in a microheterogeneous structure of cross-linked polymer. Experimental results (presented in Sects. 1.2, 1.3, and 1.4) prove the adequacy of the model; they give grounds for considering that the microheterogeneous mechanism of TFRP is substantiated quite well.

## 1.2 Polymerization Process: Stages of Formation of the Microheterogeneous Structure for Cross-Linked Polymers

### 1.2.1 Formation of Polymer Grains at the Initial Stage of Polymerization

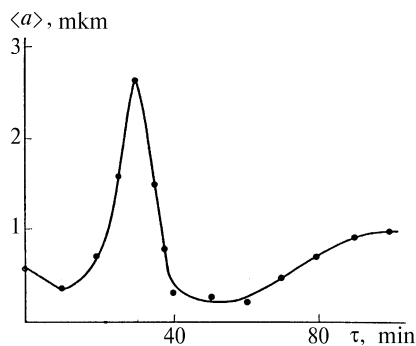
The light-scattering method enables us to study directly the generation and development of micro-nonhomogeneity and microheterogeneity of the reaction medium in the optical range of  $10^{-2}$ – $10\mu\text{m}$  at different conversions  $C$ , including the initial stage of polymerization characterized by  $C \rightarrow 0$ . Micro-nonhomogeneity (microheterogeneity) is quantitatively characterized by the variation of the light-scattering intensity  $R$  at different angles of observation  $\varphi$  and by the variation of characteristic dimensions of scattering centers  $\langle a \rangle$  calculated based on the model of small-angle scattering [11]. Comparison of the dynamics of variation of  $R$ ,  $\langle a \rangle$ , and  $C$  in the course of polymerization enabled the authors to trace the origination of micro-nonhomogeneity and then microheterogeneity of the reaction medium at the initial stage of polymerization in an example of tri(ethylene glycol) dimethacrylate (tEGdMA) oligomer polymerization [12].

From the very beginning of polymerization at  $0 < C < 5\%$  (Fig. 1.1), a certain decrease of characteristic size of scattering centers  $\langle a \rangle$  is observed (Fig. 1.2), accompanied by a concurrent slight increase of light-scattering intensity  $R$  (Fig. 1.3). Most probably, the decrease of  $\langle a \rangle$  is associated with the appearance of a large number of small scatterers in the oligomer against the background of quite large scatterers (foreign inclusions in the oligomer). These scattering centers (which are newly formed after the beginning of polymerization) could be identified with polymer coils that are responsible for the slight growth of light-scattering intensity during this period (Fig. 1.3), which in terms of order of magnitude of  $R$  corresponds to scattering of a diluted solution of polymer in a monomer [13]. At the initial stages of polymerization the reaction medium is homogeneous, although micro-nonhomogeneous: polymer coils and oligomer are not substantially different in terms of refraction index and density, as their volumetric fluctuations are



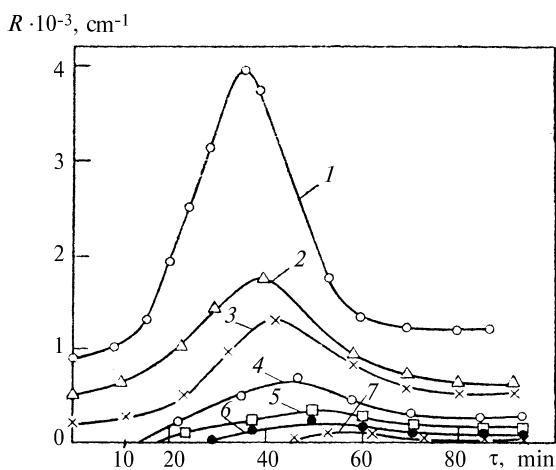
**Fig. 1.1** Integral (1) and differential (2) kinetic curves of tEGdMA photopolymerization. Temperature  $20^{\circ}\text{C}$ :  $[\text{AIBN}] = 0.03\%$  (weight)

**Fig. 1.2** Variation of average size of scattering centers in the course of tEGdMA photopolymerization. Observation angle  $\varphi = 21^\circ$ – $23^\circ$ . Temperature  $20^\circ\text{C}$ :  $[\text{AIBN}] = 0.03\%$  (weight)



responsible for the variation of light-scattering intensity value  $R$ . In the temperature range  $20^\circ$ – $80^\circ\text{C}$ , the tEGdMA oligomer is a thermodynamically good solvent of its own primary products of polymerization (so-called  $\beta$ -polymers) [14–16]. This feature provides swelling of polymer coils in the oligomer and homogenization of the reaction medium.

With the beginning of polymerization auto-acceleration, the situation is radically changed: dramatic growth of size of scattering centers  $\langle a \rangle$  and enhancement of light-scattering intensity  $R$  (see Figs. 1.1, 1.2, and 1.3) are observed. This observation is indicative of mass formation of reaction medium micro-volumes that differ dramatically from the oligomer in terms of density and refraction index. The reason for such large-scale fluctuations in reaction medium polarizability resulting from dramatic growth of  $R$  and  $\langle a \rangle$  most probably lies in mass transition of polymer coils into glass-like polymer grains as a result of local gel effect and growth of such grains. Local glass transition of quite highly cross-linked micro-volumes of



**Fig. 1.3** Variation of reduced intensity of light scattering in the course of tEGdMA photopolymerization. Observation angle  $\varphi$ : 1,  $21^\circ$ ; 2,  $30^\circ$ ; 3,  $40^\circ$ ; 4,  $58^\circ$ ; 5,  $75^\circ$ ; 6,  $80^\circ$ ; 7,  $113^\circ$ . Temperature  $20^\circ\text{C}$ :  $[\text{AIBN}] = 0.03\%$  (by weight)

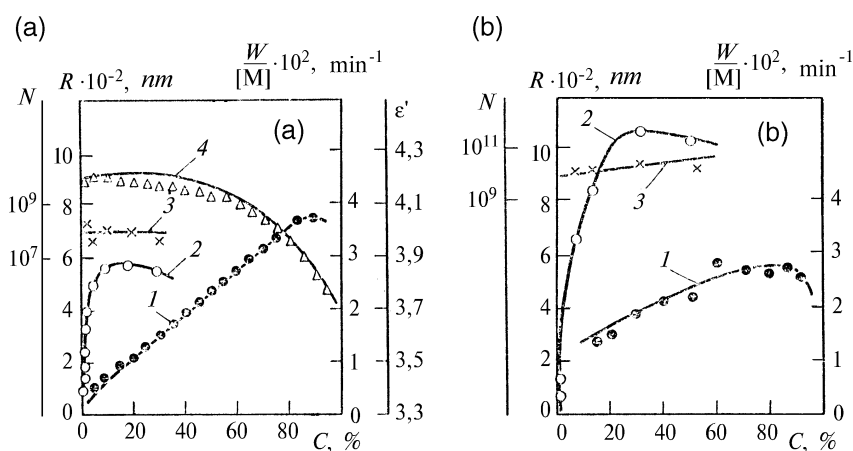
reaction medium [15] occurs in the same range of conversions, in which dramatic increase of light-scattering intensity is observed. Judging by values of  $R$ , even at low conversions, with just the beginning of polymerization auto-acceleration the micro-nonhomogeneous reaction medium becomes microheterogeneous. Such a medium is, in essence, a nano-dispersion of glass-like microgel particles, weakly bound by penetrating chains in the volume of nonreacted oligomer. The transformation of homogeneous reaction medium into a microheterogeneous one even at the initial stage of polymerization is also shown by the light-scattering method for polymerization of tEGdMA in solutions [16].

### 1.2.2 Growth of Polymer Grains During Polymerization

According to the microheterogeneous model, polymer grains that have formed even at the initial stage of polymerization are in a certain sense self-contained micro-reactors, in the surface layers of which the polymerization process becomes localized. This key point of the model needed thorough experimental substantiation.

Using the method of spectroturbidymetry, it was found (based on turbidity spectra) that actually the accumulation of new isolated particles in the reaction medium stops from the very beginning of oligo(acrylates) polymerization, and subsequent polymerization proceeds with the number of such particles practically unchanged, but with their size increased (Fig. 1.4)[17].

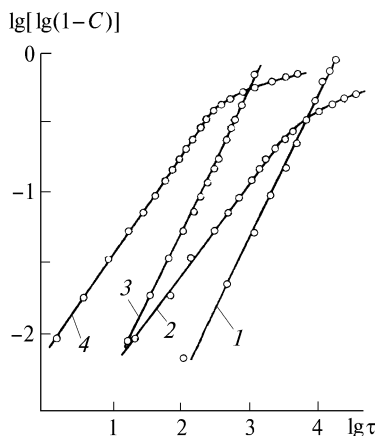
Kinetics of oligo(acrylates) polymerization is described by the Avrami equation (Fig. 1.5) [18], the derivation of which is based on the model of growing heterogeneous particles:



**Fig. 1.4** Variation of reduced polymerization rate  $W/[M]$  (1), size  $R$  (2), concentration of polymer particles  $N$  (3), and dielectric permeability  $\epsilon'$  (4) during polymerization of tEGdMA (a) and dMA-tEGPh (b) in 50% solution of benzene at 50°C

**Fig. 1.5** Dependency of dMAtEGPh conversion upon time  $\tau$  in coordinates of Avrami equation.

Polymerization conditions: 1, 2, block; 3, 4, 50% solution in benzene; benzoyl peroxide (BP), % by weight: 1, 3, 1.0; 2, 4, 0.1. Index of Avrami equation  $n$ : 1, 1.6; 2, 1.4; 3, 4, 2.1



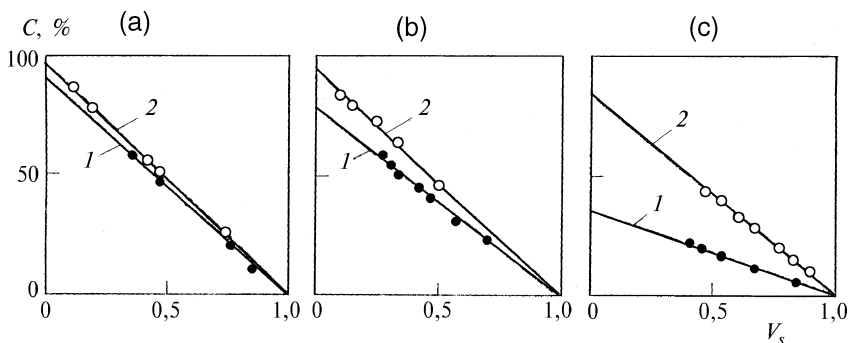
$$C = 1 - \exp(-K_t^n) \tag{1.1}$$

where  $C$  = fraction of substance that was subjected to transformation (conversion in terms of double bonds);  $K_t$  = specific rate of transformation process; and  $n$  = index, Fig. 1.6 depending on the geometric shape of growing heterogeneous particles.

An investigation of reaction medium composition as a function of conversion  $C_t$  for different types of oligo(acrylates) [19] led to the following equation:

$$C_t = C_g(1 - V_s) \tag{1.2}$$

where  $C_g$  = conversion in gel fraction and  $V_s$  = volume rating of sol fraction of polymer.



**Fig. 1.6** Dependency of sol yield upon conversion in the case of polymerization of oligo(acrylates) of different functionality  $n$ : (a) tEGdMA ( $n = 2$ ); (b) tMA-tPA ( $n = 4$ ); (c) hMA-PeA ( $n = 6$ ). Temperature °C: 1, 60; 2, 90

Besides, the value of  $C_g$  did not vary in the course of polymerization and was equal to the possible limit value of  $C_t$  at a given temperature:

$$C_g = (C_t)_{\text{lim}} = \text{const} \quad (1.3)$$

The constancy of  $C_g$  in the course of polymerization was stated based on linear character of dependency  $C_t = f(V_s)$ , while equality (1.3) was established based on the section intercepted on the ordinate by direct line in coordinates  $C_t - V_s$  with  $V_s \rightarrow 0$  (Fig. 1.6).

Since

$$C_t = C_s V_s + C_g (1 - V_s) \quad (1.4)$$

(where  $C_s$  = conversion in sol fraction), then it uniquely follows from Eqs. (1.2) and (1.4) that  $C_s = 0$ . It means that the sol fraction consists only of nonreacted initial oligo(esteracrylate) and, hence, the reaction medium during the entire polymerization process contains only two components—namely, insoluble highly cross-linked polymer (gel) with limiting conversion and nonreacted initial oligo(esteracrylate).

Because this conclusion is of key importance for experimental substantiation of the hypothesis implying growing polymer grains, the composition of sol fractions was determined using the gel chromatographic method and then analyzed for non-saturation. Indeed, the sol fraction was represented by a nonreacted oligomer. In the case when  $C_g \neq (C_t)_{\text{lim}}$  during the entire polymerization process, sol fraction also contains only an initial nonreacted oligomer [20]. This regularity is of general character, it is true for oligo(acrylates), which differ in terms of both functionality and structure of oligomer block.

According to the model forecast, polymer grains should consist of highly cross-linked glass-like cores with the limiting conversion degree (at a given temperature) and peripheral surface layers (shell) with uncompleted network structure, i.e., reaction zones, in which polymerization actually proceeds. The auto-deceleration at the final stages of TFRP is interpreted within the framework of the microheterogeneous mechanism as a result of reaction zones overlapping following the contact and accretion of polymer grains (see Sect. 1.2.3). Indeed, during the polymerization of oligo(acrylates) in solutions containing surfactant additives under the conditions excluding aggregation of polymer grains because of overlapping of their peripheral reaction zones, the authors managed to completely eliminate auto-deceleration of polymerization (Fig. 1.7) [21]. Thus, surface reaction zones of polymer grains were kinetically identified.

Information on relative size of reaction zones of polymer grains  $h/r$  (Fig. 1.8) was obtained directly from kinetic characteristics of the oligo(acrylates) polymerization process [22] based on values of  $\gamma$ :

$$\gamma = C_{\text{max.}}/C_{\text{lim}} \quad (1.5)$$

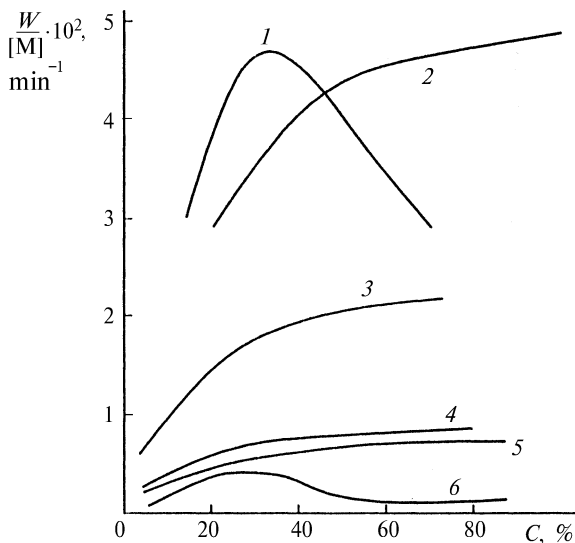
where  $C_{\text{max}}$  = conversion corresponding to maximum polymerization rate; and  $C_{\text{lim}}$  = limiting conversion that could be implemented under given conditions.

Further, the reaction medium filled with polymer grains that are in contact is approximated by a monodisperse set of spheres having radius  $r$  (see Fig. 1.8). In terms of physical meaning,  $\gamma$  is a volume fraction of polymer grains in a reaction medium at the moment of their contact. In the supposition on monodispersiveness of spherical grains, the theoretical value of  $\chi_t$  is equal to 0.64 or 0.72 for tetragonal or hexagonal packing of grains, respectively, while

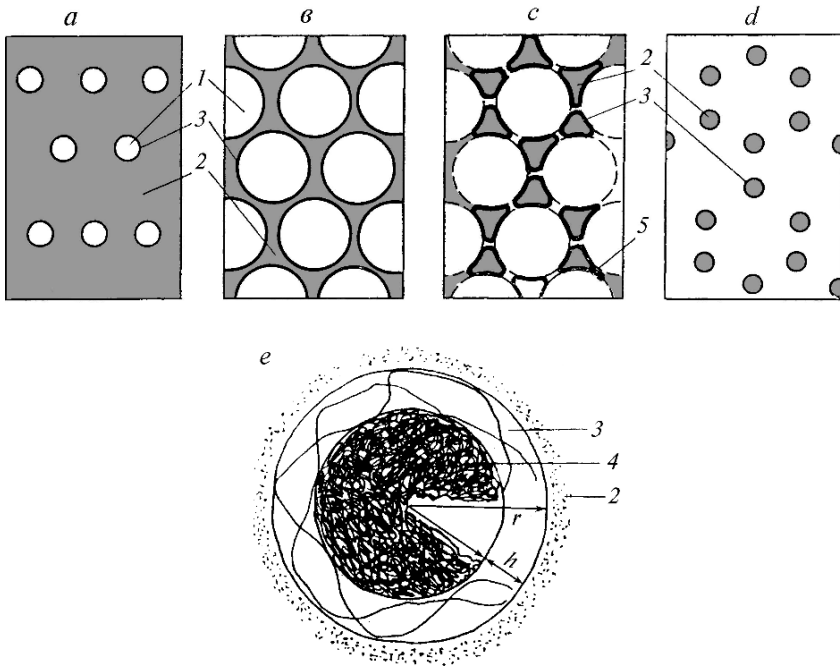
$$h/r = 1 - (\gamma/\chi_t)^{1/3} \quad (1.6)$$

It follows from the data presented in Table 1.1 that the character of variation of relative size of reaction zones (surface layers) of polymer grains  $h/r$  is determined by oligomer structure, initiator type, and polymerization temperature.

The correlation of yield of sol fraction and TFRP conversion of the type (Eq.(1.2)) enables us to suppose the following mechanism of polymer grains growth. Throughout the entire duration of the polymerization process, i.e., from formation of polymer grains until their contact and accretion (taking the constancy of their concentration in the reaction medium into account), the said process proceeds through buildup of new polymer layers over the periphery of the grains. In this process, a radial gradient of conversion from  $(C_g)_i$  at the internal side of the peripheral layer facing the grain nucleus, with  $(C_g)_i \approx (C_t)_{lim}$  to  $(C_g)_p \approx 0$  at the external side of the layer facing the interlayer of source oligomer with zero degree of transformation (see Fig. 1.8), would obviously exist in the growing peripheral layer with still incomplete network structure (i.e., in the reaction zone of the grain). The average conversion in the entire volume of grain  $C_g$  is described by the following expression (taking the peripheral layer (shell) volume



**Fig. 1.7** Kinetics of tEGdMA polymerization in solutions with stabilizing additives: 1–3, 40% solution in acetonitrile; 4–6, 30% solution in heptane. Type and concentration of additive, % (by weight): 1, 6, without additive; 2, colloxylin, 0.1; 3, linoleic acid, 0.2; 4, poly(isoprene), 0.4; 5, surfactants, 0.5



**Fig. 1.8** Formation stages (*a-d*) of microheterogeneous structure of cross-linked polymer in the course of TFRP and schematic diagram of polymer grain (*e*) at stages (*a*) and (*b*) (*e*): (*a*) formation of polymer grains; (*b*) growth of polymer grains; (*c*) contact and accretion of polymer grains; (*d*) microheterogeneous cross-linked polymer. 1, polymer grains; 2, oligomer; 3, surface layer of polymer grain (shell); 4, core of polymer grain; 5, zone of direct contact and accretion of polymer grains

into account):

$$C_g = (C_i)_{lim} \cdot (1 - V_1) + \bar{C}_1 V_1 \tag{1.7}$$

where  $\bar{C}_1$  and  $V_1$  = average conversion in the surface layer and volume of surface layer of the grain, respectively.

It is obvious that at the end of polymerization process (i.e., after the limiting conversion has been reached), the very fact of polymerization cessation is equivalent to the assertion that growing peripheral layers of grains ceased to exist and the value of  $V_1$  became zero. Consequently, at the end of polymerization the ratio of Eq. (1.7) is transformed into that of Eq. (1.4). At earlier stages of polymerization, with  $V_1 > 0$ , ratio (1.7) is true, from which it uniquely follows that  $C_g < (C_t)_{lim}$ .

In the case when the constancy of  $C_g$  and  $C_g = (C_t)_{lim}$  (see Fig. 1.6) is experimentally observed, relationships (1.2) and (1.4) do not contradict one another only on condition that  $V_1 \approx 0$  not only at the end of the polymerization process, but also throughout its entire duration. The physical meaning of this condition is as follows: the buildup of polymer grains occurs in very thin peripheral layers practically only at the very surface of grains when  $h/r < 0.1$  (see Table 1.1). When in the course of



**Table 1.1** Values  $\gamma$  and  $h/r$  for polymerization of tEGdMA and dMA-tEGPh

| Oligomer             | Initiator concentration, % (by weight) | $\gamma$ | $h/r$ | Oligomer             | Initiator concentration, % (by weight) | $\gamma$ | $h/r$ |
|----------------------|--|----------|-------|----------------------|--|----------|-------|
| Initiator AIBN, 60°C |  |          |       | Initiator DCPD, 40°C |  |          |       |
| tEGdMA               | 0.010                                  | 0.43     | 0.12  | tEGdMA               | 0.010                                  | 0.28     | 0.24  |
|                      | 0.025                                  | 0.46     | 0.10  | tEGdMA               | 0.050                                  | 0.38     | 0.16  |
|                      | 0.050                                  | 0.50     | 0.08  | tEGdMA               | 0.075                                  | 0.42     | 0.13  |
|                      | 0.075                                  | 0.53     | 0.06  | tEGdMA               | 0.100                                  | 0.45     | 0.11  |
|                      | 0.100                                  | 0.55     | 0.05  |                      |  |          |       |
| dMA-tEGPh            | 0.075                                  | 0.58     | 0.03  | dMA-tEGPh            | 0.010                                  | 0.38     | 0.16  |
|                      |  |          |       | dMA-tEGPh            | 0.050                                  | 0.40     | 0.14  |
|                      |  |          |       | dMA-tEGPh            | 0.075                                  | 0.48     | 0.09  |
|                      |  |          |       | dMA-tEGPh            | 0.100                                  | 0.62     | 0.01  |

*Note.* Given values of  $h/r$  are found from Eq. (1.7) with  $\chi_t = 0.64$  based on the assumption of more probable tetragonal packing of grains [22].

polymerization  $C_g < (C_t)_{\text{lim}}$  and when only at the end of the process, conversion in gel ( $C_g$ ) reaches the limiting value, the buildup of polymer grains occurs in quite voluminous surface layers of grains with  $h/r \geq 0.1$  (see Table 1.1).

Thus, the data set obtained through the use of independent experimental methods completely verifies the hypothesis of growing polymer grains, in the surface layers of which the polymerization process is localized.

### 1.2.3 Accretion of Polymer Grains at the Final Stages of Polymerization

According to the microheterogeneous model, at late stages of polymerization the growing polymer grains come into contact, after which polymerization accretion of discrete grains into a microheterogeneous polymer solid takes place. The monolithization of polymer grains should be accompanied by an abrupt change of properties of the polymer being formed. Indeed, a reaction medium inevitably passes through two states as the polymer grains grow. In the first state, while the size of the grains is quite small, a reaction medium represents a state of dispersion, in which the role of the dispersion phase is performed by solid highly cross-linked strong grains, while the role of continuous dispersion medium is performed by liquid nonreacted oligomer that is thickened by penetrating polymer chains (see Fig. 1.8a,b). The continuous phase should obviously have a level of strength that is close to zero level and which is characteristic of moderately concentrated solutions of polymers. The level of the properties of the polymer material on the whole in this state is preconditioned by the properties of the continuous phase; therefore, the strength should be very low whereas the permeability, in contrast, should be high.

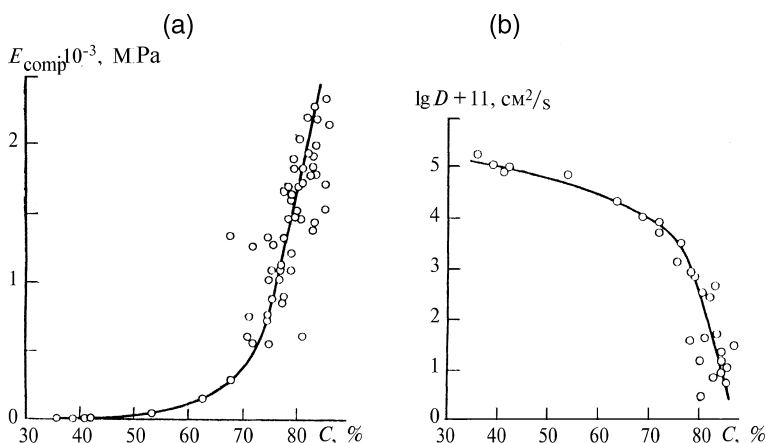
The second state of reaction medium is observed when in the course of polymer grain growth their size is increased to such an extent that they come into contact with one another and start to accrete into a single network structure as a result of polymerization in the contact zones. The oligomer (which served earlier as a continuous phase), separated by grain accretion zones into discrete micro-volumes, becomes a dispersed phase. And, vice versa, polymer grains are transformed from the dispersed phase into the continuous phase during accretion (see Fig. 1.8c). In other words, a certain critical conversion  $C_{cr}$ , which could be regarded as a phase inversion point, is reached in the course of polymerization. After  $C_{cr}$ , the presence of a structural framework composed of accreted solid highly cross-linked grains in the role of continuous phase should inevitably lead to a jump-like alteration of properties of polymer material near  $C_{cr}$ . The strength and elasticity modulus will be dramatically increased in this case, while diffusion permeability, in contrast, will be dramatically reduced; diffusion pathways, which ran over the continuous, easily permeable phase (oligomer) when  $C < C_{cr}$ , would be blocked by barely permeable barriers when  $C > C_{cr}$ .

The monolithization stage is a final stage of polymerization process, the existence of which represents a direct consequence of the microheterogeneous mechanism of TFRP. It was first experimentally discovered as a result of studying the polymerization of studying tEGdMA (triethelenglycol dimethacrylate) oligomer under widely varied conditions [23].

The degree of monolithization was evaluated by elasticity modulus of polymer in compression ( $E_{comp}$ ) and by coefficient of diffusion ( $D$ ) of a number of solvents in the polymer. A quite narrow area of conversion near  $C_{cr} \approx 75\%$ , within which dramatic, almost jump-like variation of cross-linked polymer material properties takes place, is clearly seen in Fig. 1.9 and from data presented in Table 1.2: elasticity modulus is increased almost 3.5 times (from 700 to 2,300 MPa), while the value of the diffusion coefficient is decreased under the same conditions approximately 1,000 times.

The variation of polymerization conditions—initiation method (substantial and irradiation), initiation rate, temperature, or introduction of inhibitors—does not change the above-indicated character of dependency “properties,” i.e., conversion (see also [24], pp. 69–71). It is believed that the described dependency is of universal character and should also be observed in the case of TFRP of polyunsaturated compounds of other types.

It should be pointed out that the observed abrupt change of properties within a narrow interval of conversions could not be explained by conventional gel formation because the gel point under selected conditions of tEGdMA polymerization stays within the area of low conversion values (with  $C < 1\%$ ). An abrupt change of properties is exactly a consequence of monolithization, i.e., accretion of polymer grains. The light-scattering method also records the monolithization stage as a period of sharp decline of light-scattering intensity  $R$  (see Fig. 1.3) and equally sharp reduction of characteristic dimensions of scattering centers  $\langle a \rangle$  (see Fig. 1.2). Such changes of values of  $R$  and  $\langle a \rangle$  are most probably preconditioned by changes in the nature of scattering centers resulting from reaction medium transition from



**Fig. 1.9** Dependency of elasticity modulus in case of compression  $E_{\text{comp}}$  (a) and diffusion coefficient of acetone  $D$  (b) upon conversion for tEGdMA polymerization. Polymerization conditions are given in Table 1.2

**Table 1.2** Elasticity modulus in compression  $E_{\text{comp}}$  and diffusion coefficient of acetone  $D$  for different conversion values  $C$  (polymerization of tEGdMA)

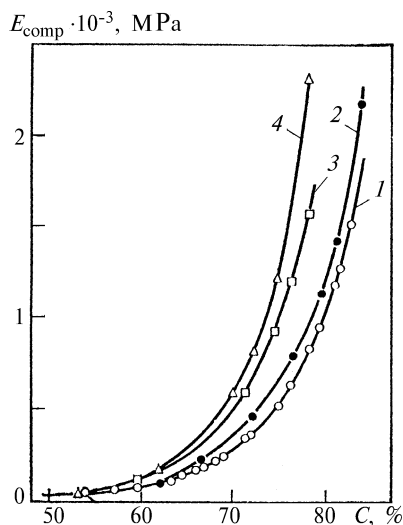
| Conditions of polymerization                                       | $C$ , % | $E_{\text{comp}}$ , MPa | $D \times 10^8$ , $\text{cm}^2/\text{s}$ |
|--|---------|-------------------------|--|
| 50°C, 240 min  | 35.8    | 5.4                     | 180                                      |
| 20°C, 150 min  | 38.8    | 10.0                    | 112                                      |
| 60°C, 180 min  | 42.0    | 13.3                    | 104                                      |
| 60°C, 240 min  | 53.3    | 50.3                    | 74                                       |
| 100°C, 25 h  | 68.0    | 297.8                   | 12                                       |
| 60°C, 61 h   | 75.0    | 564.0                   | –  |
| 60°C, 180 min + 100°C, 24 h  | 77.8    | 928.0                   | –  |
| 60°C, 365 min + 100°C, 24 h  | 77.0    | 1047.6                  | –  |
| 60°C, 180 min + $^{60}\text{Co}$ , 1 Mrad during 5 h               | 80.2    | 1736.0                  | –  |
| 60°C, 180 min + 100°C, 24 h + $^{60}\text{Co}$ , 1 Mrad during 5 h | 79.3    | 1933.7                  | 1.0                                      |
| 60°C, 61 h + 100°C, 24 h + $^{60}\text{Co}$ , 1 Mrad during 5 h    | 80.4    | 2079.0                  | –  |
| 20°C, 150 days + $^{60}\text{Co}$ , 11.5 Mrad during 10 h          | 79.0    | 1679.2                  | –  |
| 20°C, 150 days + $^{60}\text{Co}$ , 20 Mrad during 100 h           | 81.4    | 2230.6                  | –  |

*Note.* Polymerization under conditions indicated in this table was conducted using initiator AIBN ( $[\text{AIBN}] = 2 \times 10^{-2} \text{ mol/l}$ ) and inhibitor 2,4,6-trinitrotolylol (TNT) ( $[\text{TNT}] = 5 \times 10^{-2} \text{ mol/l}$ ).

the state of dispersion of growing polymer grains in a liquid oligomer (Fig. 1.8a,b) to the state at which such oligomer becomes the dispersion phase that is separated into discrete, permanently reducing volumes by zones of polymer grain accretion (see Fig. 1.8c,d).

In-depth study [25] enabled us to find that two chemically identical, but topologically different, polymerization processes proceed at the monolithization stage: one of them (characterized by low efficiency) is localized in wide intergrains layers,

**Fig. 1.10** Dependency of elasticity modulus in compression  $E_{\text{comp}}$  upon conversion: 1, without inhibitor (photopolymerization at 20°C); 2–4, without inhibitor before conversion  $C_{\text{pre}}$ , and later, with an inhibitor for different methods of postpolymerization; 2, postpolymerization for 5 h at 90°C; 3, radiation postpolymerization (dose 1 Mrad, dose rate 166 rad/s); 4, postpolymerization by photoirradiation at 20°C



whereas another (highly efficient) process proceeds in narrow zones of polymer grain contact (see Fig. 1.8). In this case efficiency is understood as an increment of the level of polymer properties that characterize monolithness; e.g., an increment of elasticity modulus  $\Delta E$ , as related to the increment of conversion  $\Delta C$  (Fig. 1.10). The physical meaning of normalizing  $\Delta E/\Delta C$  is an increment of properties level per unit of conversion.

This fundamental topological feature was experimentally determined using the selective (local) inhibition method.

Selective inhibition is based on the different sorption capacity of polymer micro-volumes with respect to molecules of inhibitor that is introduced into a partly formed polymer from the outside (these micro-volumes differ quite significantly in the partly formed polymer in terms of degree of polymer network density) [26]. Selective inhibition was carried out in the following way. The dependency between elasticity modulus at compression  $E_{\text{comp}}$  and conversion  $C$  was determined using polymer samples that were prepared under standard conditions (i.e., at 20°C, with photoinitiation in the absence of inhibitor). Curve  $E_{\text{comp}} = f(C)$  with distinct dramatic growth of value of  $E_{\text{comp}}$ , corresponding to the monolithization stage (see Fig. 1.10, curve 1), served as a reference pattern for identifying the local inhibition effect. Then, under the same standard conditions, samples of prepolymers with different conversions  $C_{\text{pre}}$  and, hence, with different elasticity moduli at compression  $E_{\text{pre}}$ , were prepared. These samples of prepolymers were saturated with vapors of stable nitroxyl radicals of 2,2,6,6-tetramethyl-piperidin-1-oxil (TEMPO), an efficient inhibitor of radical polymerization, which, diffusing into oligo(acrylates) polymers, is incapable of sorption into micro-volumes with quite highly cross-linked polymer network [26]. Following the saturation, postpolymerization of samples was carried out under the conditions of thermal, photo-, or radiation initiation until conversions  $C = C_{\text{pre}} + \Delta C$  and, hence,  $E_{\text{comp}} = E_{\text{pre}} + \Delta E$  (curves 2–4 in Fig. 1.10 and data in Table 1.3).

**Table 1.3** Variation of properties of noninhibited polymers tEGdMA upon completion of post-polymerization in the presence of inhibitor

| Prepolymer               |                       | Polymer upon completion of postpolymerization |                        |                |                        |   |
|--------------------------|-----------------------|---|------------------------|----------------|------------------------|---|
| $C_{pre}, \%$            | $E_{pre}, \text{MPa}$ | $C, \%$                                       | $E_{comp}, \text{MPa}$ | $\Delta C, \%$ | $\Delta E, \text{MPa}$ | $\Delta E/\Delta C, \text{MPa}/\%$<br>or $\Delta \text{MPa per } \Delta \%$ |
| Photopolymerization      |                       |   |                        |                |                        |   |
| 53.5                     | 50                    | 53.7  | 50                     | 0.2            | –                      | –   |
| 62.0                     | 100                   | 63.0  | 170                    | 1.0            | 70                     | 70  |
| 66.0                     | 180                   | 70.4  | 580                    | 4.4            | 400                    | 90  |
| 67.0                     | 185                   | 73.5  | 810                    | 6.5            | 950                    | 153   |
| 75.0                     | 510                   | 79.0  | 2300                   | 4.0            | 1790                   | 447   |
| Radiation polymerization |                       |   |                        |                |                        |   |
| 54.0                     | 80                    | 54.1  | 60                     | 0.1            | –                      | –   |
| 59.5                     | 75                    | 59.7  | 110                    | 0.2            | 35                     | 175   |
| 63.3                     | 115                   | 63.6  | 220                    | 0.3            | 105                    | 350   |
| 64.4                     | 140                   | 65.0  | 270                    | 0.6            | 130                    | 217   |
| 68.0                     | 210                   | 71.5  | 590                    | 3.5            | 380                    | 109   |
| 71.4                     | 350                   | 74.5  | 910                    | 3.1            | 560                    | 181   |
| 76.5                     | 630                   | 78.5  | 1560                   | 2.0            | 930                    | 465   |
| Thermal polymerization   |                       |   |                        |                |                        |   |
| 57.0                     | 60                    | 57.2  | 60                     | 0.2            | –                      | –   |
| 64.6                     | 150                   | 65.4  | 180                    | 0.8            | 30                     | 37  |
| 66.0                     | 170                   | 67.2  | 250                    | 1.2            | 80                     | 67  |
| 69.0                     | 200                   | 74.3  | 580                    | 5.3            | 320                    | 60  |
| 75.0                     | 530                   | 78.1  | 1040                   | 3.9            | 510                    | 130   |
| 71.8                     | 370                   | 76.1  | 740                    | 4.3            | 370                    | 86  |
| 81.0                     | 1180                  | 84.5  | 2150                   | 3.5            | 970                    | 277   |

Note. For conditions of postpolymerization, see Fig. 1.10.

The comparison of curves  $E_{comp} = f(C)$  (see Fig. 1.10) shows that starting from a certain critical conversion  $C_{cr} \approx 60\%$ , the elasticity modulus of samples obtained in two stages (prepolymerization without inhibitor and postpolymerization with inhibitor, curves 2–4) is always higher than that of reference samples obtained without using an inhibitor (curve 1). It is indicative of significant structural difference between samples that have been subjected to inhibition, and these structural peculiarities appear only during the postpolymerization process when the increment of conversion  $\Delta C$  is very small as compared to the initial value of  $C_{pre}$  (see Table 1.3). Indeed, the main part of the polymerization process (i.e., before  $C_{pre}$ ) proceeds under the same conditions for the samples being compared and, consequently, results in the formation of identical structures. For instance, the maximum value of  $\Delta C$  during postpolymerization was 6.5%, which was observed for  $C_{pre} = 67.0\%$ . For this sample,  $C = C_{pre} + \Delta C = 73.5\%$ , and elasticity modulus is more than twofold higher than that for the reference sample with similar conversion (curves 1 and 4 in Fig. 1.10 with  $C = 73.5\%$ ). Effects of similar scale were obtained when comparing  $E_{comp}$  of any pairs of inhibited and noninhibited (reference) samples with values of  $C$  being the same.