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Star-shaped polymers having PEO arms

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ABSTRACT

The syntheses, properties and some applications of star-shaped polymers with arms constituted of homo- or copolymers of poly(ethylene oxide) (PEO) is reviewed. The general description of the methods of syntheses, including "*arm first*" and "*core first*" procedures, of various types of star-shaped polymers is given as an introduction, without a detailed analysis of the involved chemical procedures. Then, the synthesis of star polymers (including miktoarm stars) with strictly defined as well as with varying number of arms and having cores formed from small and/or large molecules: branched, cross-linked, dendritic, etc., is described. Examples of the large number of various structures of star-shaped PEO polymers described in the literature are presented in a series of tables. Recently elaborated procedure for the synthesis of the star-shaped PEO polymers using hydroxyl terminated precursors of arms and diepoxides as core forming molecules is described in more detail because the method has a general significance and may be applied for the synthesis of a variety of star polymers. Interest in star-shaped and branched systems based on poly(ethylene oxide) (PEO) is mainly motivated by their potential applications in the biomedical and pharmaceutical areas. Therefore, the properties and applications of PEO stars are also reported, as, e.g., drug carriers, surface modifiers, and components of membranes, and/or hydrogels.

Abbreviations: ATRP, atom transfer radical polymerization; *t*BA, *tert*-butyl acrylate; *t*BMA, *tert*-butyl methacrylate; *t*Boc, *tert*-butoxycarbonyl; bpy, bipyridine; ε-CL, ε-caprolactone; D_M, dispersity (molar-mass dispersity); DAB-64, amine terminated diaminobutane poly(propylene imine) dendrimer with 64 primary amino groups; DCC, dicyclohexycarbodiimide; DGNG, diglycidyl ether of neopentyl glycol; DMAEMA, 2-(dimethylamino)ethyl methacrylate; DNA, deoxyribonucleic acid; DPE, 1,1-diphenylethylene; DVB, divinylbenzene; EGDA, ethylene glycol diacrylate; DGEG, diglycidyl ether of ethylene glycol; EGDMA, ethylene glycol dimethacrylate; EHO, 3-ethyl-3-hydroxymethyloxetane; EMA, ethyl methacrylate; EO, ethylene oxide; *f*, number of arms; *g*, branching index; GTP, group transfer polymerization; D-LA, D-lactide; D,L-LA, D,L-lactide; L-LA, L-lactide; LS, light scattering; MALDI-TOF, matrix assisted laser desorption/ionization time of flight; M_n, number-average molar mass; M_w, mass-average molar mass; M–H, Mark–Houwink; MHEG-MA, hexa(ethylene glycol) methyl ether methacrylate; MM, macromonomer; MMA, methyl methacrylate; MPEG, methyl ether of poly(ethylene glycol); MPEG-MA, poly(ethylene glycol) methyl ether methacrylate; NMR, nuclear magnetic resonance; PAA, poly(acrylic acid); PAMAM, poly(amidoamine); PB, polybutadiene; P*t*BA, poly(*tert*-butyl acrylate); P*t*BM, poly(*tert*-butyl methacrylate); PBMD, poly(3(S)-sec-butylmorpholine-2,5-dione); PCL, poly(ε-caprolactone); PDLA, poly(D-lactide); PEEGE, poly(ethoxyethyl glycidyl ether)–polyglycidol with protected –OH groups; PEG, poly(ethylene glycol); PEG-MA, poly(ethylene glycol) methacrylate; PEHO, poly(3-ethyl-3-hydroxymethyloxetane); PEI, poly(ethylene imine); PEO, poly(ethylene oxide); PGL, polyglycidol; PHB, poly(3-hydroxybutyrate); PHIC, poly(*n*-hexyl isocyanate); PI, polyisoprene; PLA, poly(D,L-lactide); PLLA, poly(L-lactide); PMA, poly(methacrylic acid); PMMA, poly(methyl methacrylate); PNIPAM, poly(*N*-isopropylacrylamide); PO, propylene oxide; PPO, poly(propylene oxide); PS, polystyrene; RAFT, reversible addition-fragmentation transfer; R_g, radius of gyration; ROP, ring opening polymerization; SEC, size exclusion chromatography; $Sn(oct)_2$, stannous octoate; SQ, silsesquioxane; T_c, crystallization temperature; T_m, melting temperature; THF, tetrahydrofuran; TMC, trimethylene carbonate; TME, trimethylol ethane [1,1,1-tris(hydroxymethyl)ethane]; TMP, trimethylol propane [1,1,1-tris(hydroxymethyl)propane]; VS, 2-(vinylsulfonyl)ethyl; X_c, degree of crystallinity.

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Contents

1. Introduction

Star-shaped polymers consist of at least three linear polymeric chains of comparable lengths radiating from one single multifunctional branched point, usually called the core or the central nodule, and which can itself be polymeric [1–3].

In a star-shaped polymer the core radius should be much smaller than the dimension, e.g., the root-mean-square end-to-end distance of the arm. If the core size is much larger, such an entity can be considered as a "nanoparticle", as its property will be dominated by the cross-linked nanometer-sized core. If the nanoparticles are approximately spherical in shape, they are referred to as "nanospheres" (cf. Fig. 1).

The main feature of star-shaped polymers, differing them from the linear analogues of identical molar masses (M_n), is their compact structure (smaller hydrodynamic volume and radius of gyration, and therefore lower viscosity) and the multiple functionality that is useful in some of their applications.

Star-shaped polymers are called homostars when all arms have the same chemical structure. Arms may be built of homo-, co-, or even terpolymers, therefore the final properties of the resulting star-shaped polymers (e.g., star-block and heterostar copolymers) may be adjusted by choosing the respective chemical structure of an arm and core, depending on the required application. Thus, star-block copolymers have each arm constituted of two homopolymeric blocks of different chemical nature, whereas heterostar copolymers have equal numbers of arms of two kinds, differing in chemical nature as well as average length, attached to the core (cf. Scheme 2) [1].

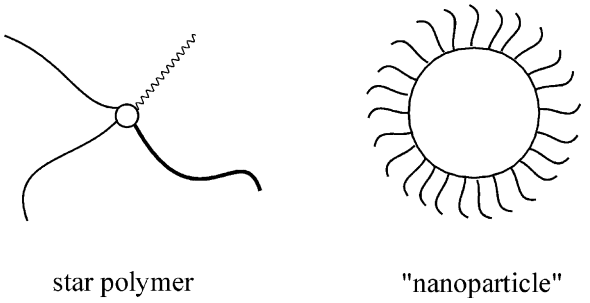

Fig. 1. Star polymer and "nanoparticle".

2. Scope of the review

Increasing interest in star-shaped polymers has been observed during the last few decades. Star-shaped