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Amphiphilic conetworks: Definition, synthesis, applications

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Abstract

The emerging field of amphiphilic conetworks (APCNs) is critically reviewed. A definition of APCNs is proposed and discussed in depth. The field of APCN science, born in 1988, is delineated and differentiated from similar constructs (e.g. interpenetrating networks, grafted networks). Among the justifications for sustained scientific/technological interest in APCNs are hosts of high-technology applications, some in commercial use and some under development. A large amount of information scattered throughout the scientific and patent literature is collected and analyzed, and the strategies for the synthesis of APCNs are identified, systematized, and evaluated. It is concluded that syntheses published to date, including those of extended-wear soft contact lenses, can be subdivided into three main groups: free radical induced polymerizations, ionic living polymerizations, and chemical combinations of hydrophilic and hydrophobic prepolymers. The strengths and weaknesses of these strategies are analyzed. Conclusions in regard to APCN synthesis and network topology are reached. The review concludes with a brief glimpse into the future.

Keywords: Amphiphilic; Network; Conetwork; Hydrogel; Interpenetrating network, Synthesis strategies; Contact lenses

Contents

Abbreviations: A, acrylate; AAc, acrylic acid; AAm, acryl amide; APCN, amphiphilic conetwork; BA, *n*-butyl acrylate; Bd, butadiene; BMA, *n*-butyl methacrylate; BzMA, benzyl methacrylate; CL, caprolactone; DMAAm, dimethyl acrylamide; DMAEMA, dimethylaminoethyl acrylamide; EtA, ethyl acrylate; GMA, 2,3 propandiol-1-methacrylate; HEA, hydroxyethyl acrylate; HEMA, hydroxyethyl methacrylate; HI, hydrophilic; HO, hydrophobic; IPN, interpenetrating network; (D,L)LA, lactic acid; $M_{c,HI}$, molecular weight of hydrophilic segment between crosslinking sites; $M_{c,HO}$, molecular weight of hydrophobic segment between crosslinking sites; MA, methacrylate; MAAc, methacrylic acid; MAAm, methacrylamide; MMA, methyl methacrylate; MW, molecular weight; MWD, molecular weight distribution; NIPAM, *N*-isopropyl acrylamide; P, poly; PBMA, poly(*n*-butyl methacrylate); PDMS, polydimethylsiloxane; PDXL, poly(1,3-dioxolane); PEG, poly(ethylene glycol); PIB, polyisobutylene; PROx, poly(2-alkyl-2-oxazoline); PSt, polystyrene; PTHF, polytetrahydrofuranp; PNVP, poly(*N*-vinyl pyrrolidone); PODVE, poly(octadecyl vinyl ether); PPO, poly(propylene oxyde); PVCL, poly(*N*-vinyl caprolactam); PεCL, poly(ε-caprolactone); SEMA, sulfoethyl methacrylate; St, styrene; T_g, glass transition temperature; THF, tetrahydrofuran; Y, $SiPh(SiH_2)OEt = $ bis[(dimethylsilyl)oxy]-[(etoxydimethylsilyl)oxy]phenylsilane.

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1. Definition

A review ought to start with a definition.

While many individuals and groups are actively engaged in amphiphilic conetwork research, a rigorous definition of this class of complex materials has not yet been proposed. To fill this gap we propose the following definition:

Amphiphilic conetworks (APCNs) are two-component networks of covalently interconnected hydrophilic/hydrophobic (HI/HO) phases of cocontinuous morphology; as such they swell both in water and hydrocarbons, and respond to changes in the medium by morphological isomerization ('smart' networks).

In the vernacular, *APCNs are hydrogels that swell in hydrocarbons.*

The three key coexisting characteristics of an APCN are: the simultaneous presence of HI and HO phases (two T_g's), covalent linkages between the phases, and phase cocontinuity (i.e. bipercolation). Phase cocontinuity is emphasized because the unique properties of APCNs cannot be explained by considering only the primary nature (HI and HO moieties) of the network segments; cocontinuity, i.e. the secondary organization or domain architecture of the system, must be part of the definition. Networks that contain dispersed, i.e. not cocontinuous, HI/HO phases are outside the scope of this definition. True, such systems may contain both HI and HO phases and exhibit two T_g's, however, since the phases are not cocontinuous, they *as a whole* do not exhibit amphiphilic character. Only if both the HI and HO phases are continuous are both water and hydrocarbons (or two solvents of very different polarities) able to permeate/percolate separately or simultaneously from edge to edge of the *entire* construct; and only then can morphological isomerization (i.e. profound phase rearrangement) occur over the entire system. Indeed, HI/HO phase cocontinuity/bipercolation renders APCNs unique among amphiphilic systems.

APCNs are smart or intelligent: they respond in a predictable manner to the medium they are in contact with. Fig. 1 helps to visualize medium-mediated morphological isomerization of an APCN. The cartoon in the center of the figure indicates an APCN in the dry state with two-phase bicontinuous morphology. In a common good solvent (top cartoon) for both the HI and HO constituents, the entire system is swollen. The lower two cartoons indicate swelling by HI and HO solvents. In the HI solvent, only the HI phase is swollen while the HO phase is collapsed; the latter wants to separate and precipitate but is unable to do so because it is covalently bound to the swollen HI phase. Importantly, in spite of the swollen HI phase, the continuity of the HO phase is maintained on account of the relative composition of the HI and HO constituents in the system, and because of the covalent bonds that connect the phases. Conversely, in the HO solvent the HO phase swells but the continuity between the collapsed HI phases is still maintained in spite of the intrusion of the HO solvent. Phase rearrangement is dynamic (reversible) upon changing the milieu (see the ⇆ in Fig. 1) and may contribute to the biocompatibility of many APCNs (see below).

Since APCNs swell in water they are hydrogels (satisfy the definition of hydrogels [1]); however, they also swell in hydrocarbons. Therefore, a more relaxed definition of APCNs is: hydrogels that swell in hydrocarbons.

A further requirement is that each and every terminus of the HI and HO segments must be connected to the network so that every chain element contributes to the load-bearing capability of the APCN. Ideally, APCNs do not contain dangling ends. In reality, a few dangling chain ends are always present at the extremities of any network (ideal systems included),