



Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Feature article

Fluorinated poly(meth)acrylate: Synthesis and properties

Wenqiang Yao, Yongjun Li^{*,**}, Xiaoyu Huang^{*}

Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:

Received 8 July 2014

Received in revised form

15 September 2014

Accepted 17 September 2014

Available online xxx

Keywords:

Fluorinated (meth)acrylate

Poly(meth)acrylate

Radical polymerization

ABSTRACT

Due to good reactivity of fluorinated (meth)acrylates with other monomers or polymer segments, fluorinated poly(meth)acrylates possess more economical and convenient synthesis routes than other fluoropolymers. This feature article initially summarizes different types of fluorinated (meth)acrylates, which can be divided into fluorinated alkyl (meth)acrylates and fluorinated aryl (meth)acrylates. Subsequently, various approaches for synthesizing fluorinated poly(meth)acrylates including random, block, graft or star copolymers are described. Conventional free radical polymerization can be used in synthesizing random copolymers, while controlled/“living” radical polymerization can provide well-defined copolymers with accurate control over molecular weight and special structures as expected. In particular, introduction of fluorinated components into as-prepared copolymers offers an alternative route to synthesize fluorinated poly(meth)acrylates which are difficult to be obtained directly via polymerization. The incorporation of fluorine can confer unique and highly desirable properties to poly(meth)acrylates such as low surface energy, thermal stability, chemical and weather resistance, low refractive index, and self-organization characteristics. Such properties are described in great details based on many recent articles.

© 2014 Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

1. Introduction

Fluorinated polymers present a number of interesting and peculiar properties provided mainly by the unique features of fluorine atom. Fluorine atom is a better atom substituting hydrogen than other heteroatoms and allows for the replacement of C–H bond with C–F bond with only minor changes in conformational mobility and steric hindrance of the resulting molecule due to its non-bulkiness. Fluoropolymers have many unique properties including high thermal, chemical, aging, and weather resistance; low dielectric constant, refractive index, surface energy, and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalis, and moisture adsorption as well as interesting oil and water repellency [1–5]. Hence, these niche polymers have been involved in many applications in spite of their high price, such as chemical resistant coatings, noncorrosive materials, antifouling coatings, and interlayer dielectrics.

However, their utility is very limited because of the incompatibility of fluorocarbons with conventional hydrocarbon

polymers. In order to further utilize many unique advantages conferred by fluorinated group, synthesis of copolymers, in which more fluorinated groups are incorporated, is essential. Recently, fluorinated poly(meth)acrylates have been the focus of numerous studies because they suit this purpose typically. On one hand, good reactivity of fluorinated (meth)acrylates with other monomers or polymer segments makes the products more economical; on the other hand, the low crystallinity and good solubility of these copolymers can improve their processability.

Copolymerization of fluorinated monomers with common hydrocarbon monomers usually results in copolymers that exhibit properties intermediate between those of parent homopolymers or enhance the range of attainable properties. For the wide specialty range and properties of transparency and resistance to deterioration by environmental effects, poly(meth)acrylates such as poly(-methyl methacrylate) (PMMA) are used in a wide variety of applications [6–10]. Poly(meth)acrylate copolymers containing fluorinated groups possess more unique and interesting characteristics, such as remarkably low surface energies, low friction coefficients, and strong incompatibility with conventional solvents [11–13].

Fluorinated poly(meth)acrylates are usually derived from monomer mixtures containing fluorinated (meth)acrylates, common hydrocarbon monomers containing one vinyl linkage or a

* Corresponding author. Tel.: +86 21 54925310; fax: +86 21 64166128.

** Corresponding author. Tel.: +86 21 54925309; fax: +86 21 664166128.

E-mail addresses: liyongjun78@mail.sioc.ac.cn (Y. Li), xyhuang@mail.sioc.ac.cn (X. Huang).

further group to induce cross-linking reactions, and occasionally ionic monomers with water solubilizing anions. With the rapid development of controlled radical polymerization, a large number of well-defined copolymers such as block copolymers based on fluorinated (meth)acrylates have emerged. Several reviews have summarized the synthesis of fluorinated copolymers [14–18], but the synthesis and properties of fluorinated poly(meth)acrylates have not been described systematically.

Extensive researches have furnished various acrylic-based materials and architectures to show their special characteristics. In order to summarize the achievements on the synthesis and properties of well-defined fluorinated copolymers, we found the time opportune to make this review on the basis of recent corresponding reports which were mostly published since 2000. In this feature article, we first describe two types of fluorinated (meth)acrylates, and then the synthesis of fluorinated poly(meth)acrylates; finally, we discuss the properties of these copolymers in detail.

2. Different fluorinated (meth)acrylate monomers

Fluorinated poly(meth)acrylates are usually obtained from copolymerization of fluorinated (meth)acrylates with common hydrocarbon monomers. Fluorinated (meth)acrylates can be divided into following two types: fluorinated alkyl (meth)acrylates and fluorinated aryl (meth)acrylates.

2.1. Fluorinated alkyl (meth)acrylates

Among fluorinated (meth)acrylates, (meth)acrylates substituted with fluorinated alkyl groups represented as $\text{CF}_3(\text{CF}_2)_m(\text{CH}_2)_n$ or $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_{m-1}(\text{CH}_2)_n$ moiety (Fig. 1) are now commercially available [16]. Monomers with trifluoromethyl at α -position of vinyl represented as methyl 2-trifluoromethylacrylate ($\text{CH}_2=\text{C}(\text{CF}_3)\text{COOCH}_3$) are also available. Most of their homopolymers are sparsely soluble in organic solvents and, in particular, polymers with a fluorinated carbon ($\text{CF}_3(\text{CF}_2)_m$) number of eight or more are generally insoluble in organic solvents, except for highly fluorinated compounds.

Researches on anionic polymerization reactivity of (meth)acrylates possessing fluoroalkyl groups in ester moieties have demonstrated that fluorine substituents have an extremely large effect on the reactivity of vinyl. For example, anionic polymerization of hexafluoroisopropyl methacrylate ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}(\text{CF}_3)_2$) initiated by triethylaluminum produced the polymer in high yields, although methyl methacrylate had a low polymerization reactivity under similar polymerization conditions because the initiation reactivity of organo-aluminums was lowered than that of organo-lithiums and organo-magnesiums [19].

Adding a spacer between acrylic group and fluorinated group could improve the properties of acrylic monomers and their polymers. To develop new liquid crystal materials, Hartman et al. synthesized a series of fluorinated acrylic monomers with a biphenyl core and hydrocarbon spacer $(\text{CH}_2)_m$ of various length ($m = 0, 6, 11$) [20]. It was illustrated that the monomer containing intermediate

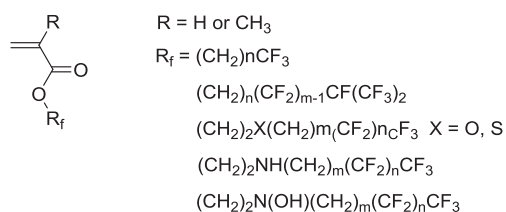


Fig. 1. Commercially available fluorinated alkyl (meth)acrylates.

length of spacer $(-\text{CH}_2)_6$ could favor the organization of rigid perfluoroalkylated biphenyl side groups in bulk in comparison with the corresponding fluorinated monomer ($m = 0$), for the self-organization of fluorinated chains could be reinforced by the lower compatibility between perfluorinated and hydrocarbon groups.

2.2. Fluorinated aryl (meth)acrylates

As an acrylic species, fluorinated aryl (meth)acrylates have been investigated for their special characters [21]. These monomers often contain an activated ester group with one or more fluorine substituents in aromatic ring, represented as pentafluorophenyl acrylate and methacrylate [22]. Pentafluorophenyl group can be substituted by aliphatic primary and secondary amines easily, so it may bring an unforeseen richness to the use of these compounds. Fluorinated aryl (meth)acrylates (Fig. 2) could be prepared by acylation of corresponding phenols with acryloyl chloride [23]. A hindered pyridine (2,6-lutidine) was used as proton acceptor in place of pyridine itself in order to prevent *in situ* polymerization of monomers. However, the obtained polymeric material after polymerizing them in bulk was insoluble and consequently no size exclusion chromatography or any other detailed characterization could be presented.

Eberhardt et al. realized the successful polymerization of pentafluorophenyl-acrylate and methacrylate yielding soluble polymeric active esters [22]. Canak et al. developed a novel fluorinated monomer of 3,5-bis(perfluorobenzyloxy)benzyl acrylate, which bore more than one fluorinated phenyl ring that contributed a more stiff structure to the polymer [24]. The fluorinated monomer and its homopolymer or copolymers could dissolve in most common solvents easily, in contrast to most fluorinated polymers.

A recent advance in the incorporation of fluorine into polymers with high performance involved a step-growth cycloaddition polymerization of trifluorovinyl aryl ether monomers to provide a kind of fluoropolymer containing perfluoro-cyclobutyl (PFCB) linkage. PFCB aryl ether-based polymer not only provides the conventional properties of fluoropolymer, but possesses many other advantages including optical transparency and improved processability. However, copolymerization of trifluorovinyl ether monomers with common vinyl monomers is very difficult due to different mechanism ($[2\pi + 2\pi]$ step-growth cyclopolymerization) and relatively high polymerization temperature ($>150^\circ\text{C}$). Tong et al. used commercially available 4-methylphenol as starting material to synthesize a novel methacrylate monomer with the incorporation of PFCB linkage as a side group [25]. Li et al. improved this method and developed a new class of PFCB-containing methacrylate monomers (Fig. 3) whose synthesis included crossing-dimerization, demethylation, and esterification using commercially available *p*-substituted phenol, tetrafluoroethylene, and methacryloyl chloride as starting materials [26,27].

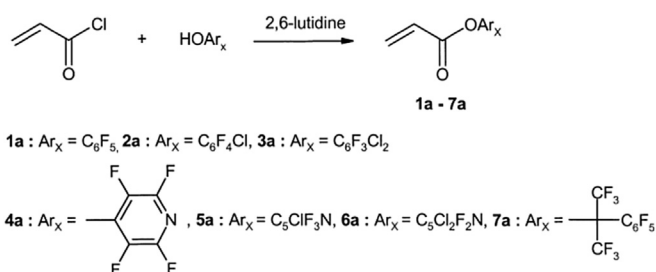


Fig. 2. Synthesis of fluorinated aryl acrylates. Reprinted with permission from Ref. [23].

Download English Version:

<https://daneshyari.com/en/article/5180729>

Download Persian Version:

<https://daneshyari.com/article/5180729>

[Daneshyari.com](https://daneshyari.com)