Polymer 102 (2016) 183–191

Contents lists available at ScienceDirect

Polymer

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

Synthesis of narrow molecular weight distribution polyvinyl acetate by gamma–rays initiated RAFT/MADIX miniemulsion polymerization

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ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form
31 August 2016
Accepted 2 September 2016
Available online 4 September 2016

Keywords:
RAFT/MADIX technique
Gamma radiation
Miniemulsion polymerization

ABSTRACT

For the first time, conventional and controlled miniemulsion polymerization of vinyl acetate (VAc) was performed using gamma radiation as alternative source of initiation. Reversible addition-fragmentation chain transfer/macromolecular design via interchange of xanthates (RAFT/MADIX) technique was applied to control the polymerization process. For this purpose, S-2-cyano-2-propyl-O-ethyl xanthate (**C**TA) was used as chain transfer agent. To illustrate the advantages of using gamma radiation instead of other initiation sources, we compared gamma radiation and the 2,2′-azobis(isobutyronitrile) (AIBN) as initiators in the polymerization mediated by RAFT/MADIX technique. Compared with conventional miniemulsion polymerization, the controlled polymerization process allowed obtaining monomodal molecular weight distribution**s** and a significant control over the molecular weight distribution. The miniemulsions showed colloidal stability during polymerization and stable latices were obtained in a short reaction time with high conversion. Gamma radiation demonstrated to be a better initiator than AIBN for the miniemulsion polymerization of VAc, mediated by RAFT/MADIX.

1. Introduction

Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization is a well-known reversible deactivation radical polymerization method that has been broadly studied due to its ability to create polymeric structures with a controlled molecular weight, low dispersity, and well-defined architecture [1–4]. RAFT polymerization has had an immense impact regarding control of the free radical polymerization of vinyl monomers under a wide variety of reaction conditions, and consequently it has become one of the most exploited controlled radical polymerization techniques. Specifically, RAFT polymerization incorporates a thiocarbonylthio compound that acts as chain transfer agent in a reversible addition–fragmentation transfer mechanism (Fig. 1) [5–7]. On the other hand, macromolecular design via interchange of xanthates (MADIX) is a process developed to control radical polymerization through the use of xanthates that displays the same mechanism of addition fragmentation than RAFT [8–10]. Even though MADIX is the correct term that should be used when xanthates are employed, RAFT is the more general term commonly found in the literature.

Although thermal chemical initiators, such as azo-compounds, have been commonly employed to initiate RAFT polymerization, other sources of initiation for instance, gamma radiation [11,12], UV radiation [13], microwave [14,15] or visible light [16,17] can also be used. It has been demonstrated, that when gamma radiation is used as an initiator in RAFT polymerization processes, polymers with living characteristics and interesting polymeric structures (e.g., graft copolymers) can be obtained [18–21]. Gamma radiation is high-energy ionizing radiation that has been extensively used in the modification of polymers due to its ability to generate radical

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http://dx.doi.org/10.1016/j.polymer.2016.09.004
0032-3861/

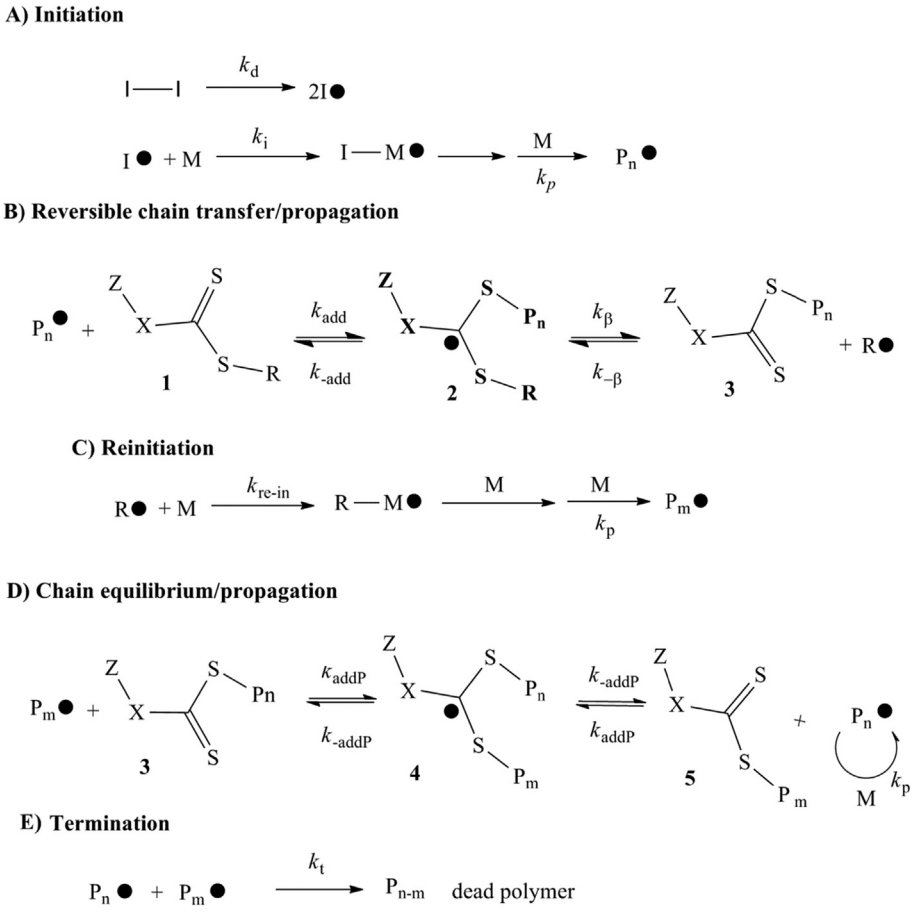

Fig. 1. RAFT mechanism.

species within a polymeric structure [22–24]. In addition, gamma radiation is an attractive option to initiate free radical polymerization because it offers clear advantages over chemical initiators, such as the possibility to carry out the reactions at ambient temperature and with short reaction times, and it greatly simplifies work up conditions by obtaining polymers with high conversion yields and purity.

Poly(vinyl acetate) (PVAc) is a thermoplastic and amorphous polymer that is employed in a large variety of industrial applications, including: adhesives, paints, color enhancers and concrete additives [25]. PVAc is also combined with other polymers to obtain composites, blends, and copolymers, for instance: ethylene-co-vinyl acetate (EVA), which is a flexible film for packaging. Moreover, the hydrolysis of PVAc is also of great interest because it allows producing poly(vinyl alcohol), which is a biodegradable polymer extensively used in the pharmaceutical and biomedical fields [26]. PVAc is produced by the free radical polymerization of vinyl acetate (VAc), a reaction that proceeds with very limited control, and undergoes chain transfer to polymer and monomer due to the high reactivity of the VAc propagating radicals. Under these conditions, PVAc with side-chain branches and a high dispersity is commonly obtained. However, for special applications in food and medical fields, it would be desirable to obtain PVAc with a narrow dispersity or a well-defined structure, which is indeed a big task, if conventional free-radical polymerization is used.

In recent years, different studies have been reported on the application of RAFT polymerization to overcome the problems associated with conventional free-radical polymerization of VAc. Xanthates and thiocarbamates have been demonstrated to be efficient chain transfer agents to perform the controlled radical polymerization of VAc either in homogeneous media (bulk and solution) [13,27–31] or heterogeneous media (suspension, emulsion, miniemulsión or microemulsion) [32–36]. It is worth noting, that only one of these works has examined the use of gamma radiation as an alternative source of initiation [30], and none have evaluated the possibility of performing RAFT/MADIX miniemulsion polymerization of VAc by gamma radiation.

A miniemulsion can be defined as a colloidal dispersion that consists of small oil droplets dispersed in water with a diameter between 50 and 500 nm and stabilized by a surfactant that reduces coalescence and provides colloidal stability to the miniemulsion. The miniemulsion is prepared by a homogenization process involving the use of a high pressure homogenizer or an ultrasonicator that produces narrowly size-distributed oil droplets which contain a coestabilizer to retard diffusional degradation (Ostwald ripening).

Miniemulsion polymerization [37–39] is a variation of emulsion polymerization and, consequently, both have some characteristics in common such as the presence of a compartmentalization effect, low viscosity, good heat transfer, and a solvent-free organic process with this last point being particularly attractive from an industrial standpoint. However, in miniemulsion polymerization, the small monomer droplets dispersed in water act as individual reactors where fast reaction rates are reached. Because of droplet nucleation is the predominant mechanism in particle nucleation, the diffusion of monomer from the monomer droplets to the polymeric particles, as it occurs in emulsion polymerization, can be ruled out.

Although emulsion polymerization is a process extensively