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An evaluation of the effectiveness of continuous thin film processing in a spinning disc reactor for bulk free-radical photo-copolymerisation

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ABSTRACT

This paper reports on UV-initiated free-radical copolymerisation of vinyl acetate with *n*-butyl acrylate (VAc-BA) under conditions of thin film flow in a spinning disc reactor (SDR). Almost 40% overall monomer conversion can be achieved in under 5 s under optimised operating conditions in the SDR, with controlled molecular weight properties of the copolymer, highlighting the good levels of mixing in the film. Residence time on the SDR is a limiting factor in the extent of conversion achievable in a single pass. Comparison with a static film demonstrates the superiority of the SDR in maintaining a high overall rate of polymerisation. Composition of the copolymer formed in the SDR indicates that, due to its plug flow behaviour, the SDR cannot address the inherent problem of compositional drift.

We have shown that efficiency of light absorption is dictated by conditions favouring longest UV exposure times, rather than thinner films on the disc. Initiator decomposition efficiency, an important consideration in the overall rate of the co-polymerisation, is enhanced by lower fluid flowrates. This study highlights the promising technology offered by the SDR in combination with UV irradiation for the exploitation of photo-copolymerisation as a viable method for bulk copolymer synthesis.

1. Introduction

Copolymerisation is a powerful method for introducing systematic changes in polymer properties. It is hugely important from a commercial standpoint. The ability to incorporate into the same polymer molecule, in varying proportions, monomer units having diverse physical and/or chemical properties allows for enormous flexibility in the manufacture of copolymers with narrowly defined properties. For example, the vinyl acetate–butyl acrylate (VAc–BA) copolymer finds application as an architectural coating, sealant and adhesive [1,2].

The bulk method of copolymerisation is a potentially environmentally friendly processing route. Avoiding the use of additives such as solvents, surfactants or suspension stabilisers means that less downstream processing is required, thereby saving money and energy. Obviously, the disposal or storage of these potentially environmentally harmful materials upon purification of the final polymer product becomes less of an issue. It also means that the yield of product per volume of reactor is greater than for other common production techniques such as emulsion polymerisation. However, in spite of the described advantages of the bulk polymerisation process, only few polymers such as polyethylene and poly(methyl methacrylate) [3] and high-impact polystyrene [4] are manufactured using this method, usually in a number of stages and in specialised tower reactors at high conversions [3,4]. This method of polymerisation is therefore generally unsound for producing high quality, high conversion polymers in conventionally employed large stirred tank reactors which suffer from limited heat transfer and mixing capacities, more so in the presence of highly viscous reaction media.

The emergence of UV radiation as an inexpensive and efficient alternative technique of initiating polymerisation has benefited numerous processes such as industrial cross-linking processes, curing applications such as dental restorations, optoelectronics and adhesive manufacturing [3] as well as surface grafting reactions in order to modify polymer surfaces [5,6]. Moreover, a large number of investigative kinetic studies are performed using photoinitiators since the start and end times of initiation and, thus, polymerisation, can be exactly defined [7]. UV radiation has the potential to introduce numerous savings resulting from the high reaction rates obtainable coupled with reduced energy requirements [8]. It is a rapid process that can be controlled much more effectively than thermal initiation by simple variation of the incident radiation intensity [3]. Furthermore, the fact that photo-initiation can take place over a wide temperature range provides a greater degree of tacticity control of the polymer product [3,9]. There is also

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Nomenclature

A_{disc}	surface area of rotating disc (m^2)
c	speed of light ($\mathrm{m\,s^{-1}}$)
C, $\bar{C}$	concentration of light absorbing species ($\mathrm{mol\,L^{-1}}$)
f	frequency of UV radiation ($\mathrm{s^{-1}}$)
F_i	mole fraction of monomer i in the copolymer
h	Planck's constant (J s)
I	intensity of transmitted light ($\mathrm{mW/cm^2}$)
I_0	incident light intensity ($\mathrm{mW/cm^2}$ or mol photons $10^{-3}\,\mathrm{cm^{-2}\,s^{-1}}$)
$\bar{I}_{\mathrm{a}}$	average absorbed light intensity across the film thickness (mol photons $10^{-3}\,\mathrm{cm^{-2}\,s^{-1}}$)
$I_{\mathrm{a},\mathrm{disc}}$	light energy absorbed over whole disc area in one disc pass (mol photons)
K	consistency index ($\mathrm{Pa\,s^n}$)
l	film thickness (cm)
M_{DMPA}	molecular mass of DMPA ($\mathrm{g\,mol^{-1}}$)
M_n	number average molecular weight ($\mathrm{g\,mol^{-1}}$)
n	flow behaviour index
N_{A}	Avogadro's number ($\mathrm{mol^{-1}}$)
n_i, n_j	number of moles of components i, j, in the feed mixture
$[\mathrm{PI}]_0$	initial initiator concentration (% w/w)
$[\mathrm{PI}]_{\mathrm{disc}}$	amount of initiator present on disc surface (mol)
Q	feed flowrate ($\mathrm{m^3\,s^{-1}}$)
r	radial distance from centre of disc (m)
R_{p}	polymerisation rate ($\mathrm{mol\,L^{-1}\,s^{-1}}$)
t	time (s)
t_{res}	mean residence time on rotating disc (s)
V_r	film radial velocity ($\mathrm{m\,s^{-1}}$)
x	individual monomer conversion (%)
X	overall conversion to copolymer (%)
z	vertical distance from disc surface (m)

Greek symbols

α	absorption coefficient ($\mathrm{L\,mol^{-1}\,cm^{-1}}$)
$\dot{\gamma}(r,z)$	shear rate at radial position r and vertical distance z ($\mathrm{s^{-1}}$)
φ	quantum yield of initiation (assumed to be 0.6 [35])
λ	incident light wavelength (m)
μ_{a}	apparent viscosity (Pa s)
ν	kinematic viscosity of polymerising film ($\mathrm{m^2\,s^{-1}}$)
ρ	density ($\mathrm{g\,L^{-1}}$)
ω	angular velocity on rotating disc ($\mathrm{rad\,s^{-1}}$)

Abbreviations

BA	butyl acrylate
DMPA	2-2-dimethoxyphenylacetophenone
MEHQ	4-methoxyphenol
VAc	vinyl acetate

the added benefit that temperature changes may be implemented without adversely affecting the initiation step. This option of decoupling the effects of temperature on the initiation and propagation rates is not available in a thermally initiated system. Because thermal initiators often have a temperature range within which they work optimally, the operating temperature has to be selected primarily on that basis and may not be the ideal temperature for the overall polymerisation process.

The main challenges with employing this method of initiation in conventional stirred tank polymerisers are related to UV penetration into the polymerising mixture, which is governed by the optical properties of the absorbing material and by its concentration according to the Beer–Lambert law. UV penetration depths can be significantly limited to a few millimetres into the mixture especially at high concentrations of the absorbing species [10]. This may result in inefficient use of the large reactor volumes typically employed in commercial scale stirred tank reactors unless adequate stirring is provided to allow constant recirculation of the fresh absorbing species near the UV source [11]. The immersion-well batch reactor [11] commonly used for photochemical processes is based on these principles. One potential problem in such reactors is that unusually long processing times may be required, more so in viscous media, for photochemical reactions to reach completion due to the additional recirculation times. Improved designs of photochemical reactors, where the efficiency of light absorption is enhanced mainly through thin film formation, have been suggested and they include falling-film reactors where a thin film flows down surfaces of various configurations under gravity [12,13] and continuous flow microreactors [10]. However, limited information is available in the literature on applications of these improved versions of photo-reactors for bulk homo- or co-polymerisation processes [14] which are renowned for the challenges involved in their handling due to their typically high viscosities.

The spinning disc reactor is a continuous flow reactor technology which offers significant benefits for the exploitation of photopolymerisation using the bulk procedure. Not only does the centrifugal force enable relatively easy flow of viscous polymer mixtures but the viscosities can also be reduced under the high shear rates in the film. Moreover, the efficiency of UV-initiation can be enhanced via extremely efficient penetration of the thin films generated on the disc surface. The ability to vary the thickness of the film by controlling the disc rotational speed is a bonus feature which is not available in the falling film reactors operating under gravity. Past studies on the SDR [15] have demonstrated that significant levels of conversion (>90%) can be attained for fast bulk *homo*polymerisations (*n*-butyl acrylate) employing UV radiation as a means of initiating the reaction. More recently, a study involving UV-induced graft copolymerisation of acrylic acid and vinyl-oxybutyl-polyethylene glycol in the SDR has reported 70% conversion of acrylic acid in 2 passes on a 20 cm diameter disc [16]. Additionally, molecular weight distributions (MWDs) have been observed to be narrow, even at high conversion, suggesting that the excellent mixing reduces or eliminates the gel effect typically observed in conventional high-viscosity polymerisation processes [15,16]. In this present contribution, we address photo-induced bulk co-polymerisation in the SDR, on which no work has been reported to date. The unique challenges in controlling the formation and properties of co-polymers in general make this study all the more worthwhile.

2. Experimental work

The performance of a spinning disc reactor (SDR) for the bulk free-radical photo-copolymerisation of vinyl acetate with butyl acrylate at 75 °C (348 K) was studied and compared with a static film process. With this comparison, our objective was to investigate the effect of film mixing on the copolymerisation rate and the copolymer properties. The choice of monomers used was influenced by two major factors. Primarily, the rate constant for propagation of this co-monomer system is relatively high – approximately 17,060 $\mathrm{L\,mol^{-1}\,s^{-1}}$ at 348 K [17] – so that polymerisation should still be able to occur even during the short residence times offered on the SDR. Secondly, there is a large difference between the reactivity ratios of these two monomers ($r_{\mathrm{BA}} = 5.93$ and $r_{\mathrm{VAc}} = 0.026$), such that any improvement in copolymer homogeneity as compared to the static film system should be much