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Cellulose acetate graft copolymers with nano-structured architectures: Application to the purification of bio-fuels by pervaporation

M. Billy [a], A. Ranzani Da Costa [a], P. Lochon [a], R. Clément [a], M. Dresch [b], A. Jonquières [a,*]

[a] Laboratoire de Chimie Physique Macromoléculaire, UMR CRNS-INPL 7568, Nancy Université, ENSIC, 1 rue Grandville, BP 20451, 54 001 Nancy Cedex, France
[b] ADEME, 20 avenue du Grésillé, BP 90406, 49 004 Angers Cedex, France

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ABSTRACT

In Europe, ethyl *tert*-butyl ether (ETBE) is currently considered as one of the most promising bio-fuels when it is obtained from bio-ethanol. Nevertheless, its industrial synthesis process leads to an azeotropic mixture containing 20 wt% of ethanol which has to be removed for fuel applications. In this work, new graft copolymers cellulose acetate-*g*-poly(methyl diethylene glycol methacrylate) are considered for the purification of ETBE by pervaporation. Two families of graft copolymers were investigated with almost the same copolymer graft contents but short or long highly permeable grafts. Their properties are discussed in terms of structure–property relationships for the sorption and pervaporation of the targeted azeotropic mixture. It is shown that the sorption properties are mainly governed by the copolymer graft content. On the other hand, the pervaporation features are strongly influenced by the copolymer graft content and architecture. For the same copolymer graft contents, it appears that the copolymers with short grafts are more selective and less permeable than the copolymers with long grafts. This difference in permeation behaviour is ascribed to different copolymer microstructures. The less segregated short grafts are more constrained within the rigid cellulose acetate matrix and lead to pervaporation separation factors that are twice those of the corresponding copolymers with long grafts. A comparison with the related literature results also shows that these graft copolymers are amongst the best materials so far reported for the separation of the azeotropic mixture ETBE/EtOH and this approach appears really promising for the design of a wide range of new copolymers with outstanding features for this application.

1. Introduction

Alkyl *tert*-butyl ethers are highly efficient fuel octane enhancers widely used worldwide in replacement of former lead derivatives which have been banned from gasoline for environmental protection. In Europe, ethyl *tert*-butyl ether (ETBE) is largely preferred to methyl *tert*-butyl ether (MTBE) because the former is much better biodegradable than the latter thanks to the presence of a hydrogen atom in β-position to the ether group [1,2]. ETBE is usually obtained from the reaction of a large excess of ethanol with isobutene in order to shift the corresponding reaction equilibrium towards ether production. When ETBE is obtained from bio-ethanol, it is also currently considered as one of the most promising bio-fuels. Following the general recommendations of the French governmental commission for sustainable development of bio-fuels in France [3], the French ETBE production capacity has almost doubled over the past 10 years, up to a current capacity exceeding 400,000 tons a year.

Nevertheless, the separation of the azeotropic mixture ETBE/EtOH (80/20 wt%) is a true challenge in the industrial synthesis process of ETBE [4]. The conventional separation process involves a ternary or "azeotropic" distillation which combines three distillation towers with high cost in terms of time and energy. Pervaporation, alone or in hybrid processes [5], could be a really interesting alternative to this conventional process for alkyl *tert*-butyl ether purification as reported by several teams worldwide [6–9].

Amongst the organo-selective polymers so far reported for removing alcohol from ethyl *tert*-butyl ether by pervaporation, cellulosic esters have been widely used for membrane applications [10,11] and they have displayed quite outstanding properties for this particular separation as shown by the data reported by Nguyen et al. [12] (Table 1). Cellulose acetate appears to have a quasi-infinite selectivity towards ethanol with a pervaporate ethanol content very close to 100%. Nevertheless, the pervaporation flux of cellulose acetate appears far too low for an industrial application. In the same conditions, the pervaporation flux of cellulose proprionate is almost one order of magnitude higher than that of cellulose acetate and the pervaporate still contains 96 wt% of ethanol. Still increasing the hydrophobic character of the ester

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* Corresponding author. Tel.: +33 3 83 17 50 29; fax: +33 3 83 37 99 77.
E-mail address: anne.jonquieres@ensic.inpl-nancy.fr (A. Jonquières).

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Table 1
Typical pervaporation properties of cellulosic esters and other related membranes for the separation of the azeotropic mixture ETBE/EtOH (80/20%, w/w). Normalized flux for a reference membrane thickness of 5 μm. C': ethanol weight fraction in pervaporate.

Membrane	T (°C)	$J_{\text{normalized}}$ (kg/(m^2 h))	C'	α_{PV}	Reference
Cellulosic esters					
CA	40	0.08	≈1	≈∞	[12]
CAP	40	0.70	0.96	96.0	[12]
CAB	40	1.7	0.90	36.0	[12]
Cellulosic blends					
CAB-CAP (10–90%, w/w)	40	0.6	0.967	117.2	[13]
CAB-CAP (20–80%, w/w)	40	0.7	0.957	89.0	[13]
CAB-CAP (40–6%, w/w)	40	1.3	0.933	55.7	[13]
CAB-CAP (50–50%, w/w)	40	3.0	0.907	39.0	[13]
CAP-PAA (95–5%, w/w)	40	0.82	0.964	107.1	[15]
CAP-PAA (80–20%, w/w)	40	0.87	0.952	79.3	[15]
CAP-PAA (70–30%, w/w)	40	0.88	0.95	76.0	[15]
CA-P(VP-co-VAc) (40–60%, w/w)	40	2.3	0.86	24.6	[14]
CA- P(VP-co-VAc) (60–40%, w/w)	40	0.8	0.975	156.0	[14]
CA- P(VP-co-VAc) (95–5%, w/w)	40	0.3	0.98	196.0	[14]
CAP-P(VP-co-AA) (95–5%, w/w)	40	0.52	0.977	169.9	[16]
CAP-P(VP-co-AA) (95–5%, w/w)	50	0.87	0.966	113.6	[16]
CAP-P(VP-co-AA) (95–5 w/w%)	60	1.24	0.959	93.6	[16]
Cellulosic semi-IPNs					
CA-EGDMA (50–50%, mol/mol)	40	0.02	1	≈∞	[12]
CAP-EGDMA (50–50%, mol/mol)	40	2.0	0.96	96.0	[12]
CAB-EGDMA (50–50%, mol/mol)	40	4.4	0.895	34.1	[12]
CA-PEG200DMA (50–50%, mol/mol)	40	0.02	1	≈∞	[12]
CA-TEEMA.PEG200DMA (50–25.25%, mol/mol)	40	0.50	0.97	129.3	[12]
CA-TEEMA.PEG600DMA (50–25.25%, mol/mol)	40	0.90	0.96	96.0	[12]

CA: cellulose acetate, CAP: cellulose acetate propionate, CAB: cellulose acetate butyrate, PAA: poly(acrylic acid), P(VP-co-Vac): poly(vinylpyrrolidone-co-(vinyl acetate)), P(VP-co-AA): poly(vinylpyrrolidone-co-(acrylic acid)), EGDMA: ethyleneglycol dimethacrylate, PEG200DMA: polyethyleneglycol 200 dimethacrylate, PEG600DMA: polyethyleneglycol 600 dimethacrylate, TEEMA: triethoxy ethyl methacrylate.

group leads to a comparatively low increase in flux in detriment to the selectivity which decreases sharply for cellulose butyrate. Blends of cellulose butyrate and propionate have also been reported by Schaetzel and coworkers for this separation with interesting fluxes but significantly decreased pervaporate ethanol contents compared with cellulose acetate [13] (Table 1). From these results, it readily appears that plasticizing cellulose acetate would be very interesting for the targeted application if its selectivity could be kept in the very high range at the same time. Nguyen et al. and Schaetzel and coworkers have already shown that cellulose esters plasticizing by poly(meth)acrylic polymers in blends can lead to a very strong permeability increase while still keeping an excellent selectivity [12,14–16]. Nevertheless, it has also been sometimes reported that the slow extraction of the poly(meth)acrylic polymers, very well accounted for by the reptation De Gennes theory, was responsible for a slow decrease of the pervaporation features over time [17]. Another interesting related approach was the design of semi-interpenetrating networks (semi-IPNs) based on cellulose acetate and cross-linked poly(meth)acrylate networks obtained by photopolymerization [12,18]. The cross-linking clearly avoided the former extraction but the whole system was more difficult to implement and the corresponding membranes showed strong anisotropy.

This new paper reports on the properties of new cellulose acetate graft copolymers we have recently obtained by controlled radical polymerization [19]. Fig. 1 shows the principle of their synthesis in two steps. In a first step, cellulose acetate was modified chemically to introduce initiator groups. The second step consisted of grafting a methacrylic monomer by Atom Transfer Radical Polymerization (ATRP). This new approach should combine all the advantages reported in the former works (i.e. efficient internal plasticization, high flux and selectivity) and avoid the corresponding former drawbacks like polymethacrylic chain extraction or strong membrane anisotropy. The graft copolymers contained between 0 and 50 wt% of poly(methyl diethylene glycol methacrylate) grafts. Two families of copolymers were investigated with almost the same graft weight fractions but long or short grafts, thus corresponding to different architectures (Table 2).

In this work, the sorption and pervaporation properties are analyzed for both families of graft copolymers during the separation of the azeotropic mixture ETBE/EtOH. One of the questions underlying the motivation for this work was whether graft copolymers with almost the same graft weight fractions but different architectures would behave similarly or show significant differences in permeability.

2. Experimental

2.1. Materials

Prior to use, cellulose acetate (CA, Fluka, acetyl content: 40 wt%, MW = 52,000 g/mol) was dissolved in 2-butanone (Aldrich) then precipitated in a large excess of absolute ethanol and dried for five days in vacuum at 60 °C. The synthesis of the graft copolymers CA-*g*-poly(methyl diethylene glycol methacrylate) was reported elsewhere [19]. For the sake of simplicity, the different copolymers are abbreviated as follows: GSX and GLX for copolymers with *X* wt% of short or long grafts, respectively (Table 2).

Absolute ethanol (EtOH, Aldrich) was used without further purification. Its water content determined by gas chromatography

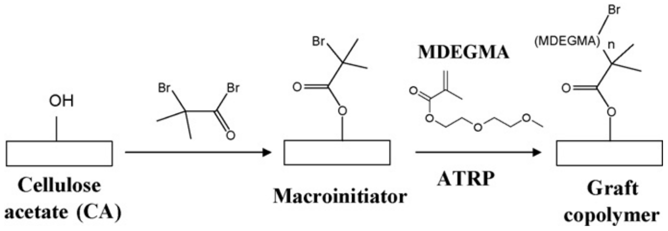

Fig. 1. Synthesis principle of the graft copolymers cellulose acetate-*g*-poly(MDEGMA) with different architectures.