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Size-exclusion simulated moving bed for separating organophosphorus flame retardants from a polymer

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ABSTRACT

Over 500,000 t of flame retardants in electronic wastes are consigned to landfills each year. A room-temperature, size-exclusion simulated moving bed (SEC-SMB) was developed to recover high purity (>99%) flame retardants with high yield (>99%). The SSWD method for ternary mixtures was developed for SEC-SMB. Fourteen decision variables were optimized to obtain the lowest separation cost within 1 min. The estimated cost is less than 10% of the purchase cost of the flame retardants. The estimated cost of the optimized SEC-SMB is less than 3% of that of a conventional batch SEC processes. Fast start-up methods were developed to reduce the SMB start-up time by more than 18-fold. SEC-SMB can be an economical method for separating small molecules from polymers.

1. Introduction

Over 50 million tons of waste electrical and electronic equipment (WEEE) are generated worldwide each year and they are growing at a rate of 3–5% per year [1–5]. Polymeric materials make up about one third of that weight [6,7]. The United States Environmental Protection Agency estimated that less than 20% of the wastes, mostly metals and glass, are recycled [8,9]. The rest of the wastes are currently stored in landfills or scattered in the oceans around the world [10,11]. Slow degradation of the polymers releases toxic chemicals, which potentially endanger wildlife and affect our food supply [12,13]. Recovering polymers and valuable chemicals from the wastes can reduce these environmental hazards and the amount of raw materials and energy required for synthesis.

Recovery of high-purity polymers from a polymer waste is challenging because many polymers have similar physical properties and broad, overlapping molecular weight (MW) distributions. Single solvents do not have the selectivity to recover high-purity polymers with high yield. A room-temperature, mixed-solvent process, Sequential Extraction for Polymer Recovery (SEPoR), was developed to recover polymers from wastes [14,15]. The solvent compositions are designed using a combination of Hansen Solubility Parameter (HSP) theory, gradient polymer elution chromatography (GPEC), and solubility tests. SEPoR has already been developed for recovering high-purity (>99%) polycarbonates (PCs) with high (>95%) yield from a computer waste. SEPoR uses 84% less energy than chemical synthesis and can reduce CO_2 emissions and reduce raw materials from petroleum used to synthesize virgin polymers [15]. Poly(acrylonitrile-co-butadiene-co-styrene) (ABS) is removed as a separate, solid product. Flame retardants (FRs) and a polymer, poly(styrene-co-acrylonitrile) (SAN), are discharged in a side stream of 50/50 (vol.%) acetone (ACE)/dichloromethane (DCM). Recovery of the FRs and SAN from the side stream is economically desirable and beneficial to the environment, and it is the focus of this study.

Flame retardants, such as resorcinol bis-diphenylphosphate (RDP) and bisphenol A bis-diphenylphosphate (BPADP), are added to polymers in order to inhibit the spread of flames in case of fire [16,17]. Many flame retardants containing bromine or other halogens are being preplaced by organophosphorus FRs, which are safer and more environmentally benign [18,19]. This study focuses on the recovery of RDP (575–4025 Da), BPADP (693 Da), and SAN (50,000–150,000 Da) from one of the side streams of the SEPoR process for PC recovery, Fig. 1. The molecular structures for the FRs and SAN are shown in Table 1.

The FRs are the most valuable components in the polymer wastes by weight. Polymers in WEEE have 10 wt.% or more FRs.

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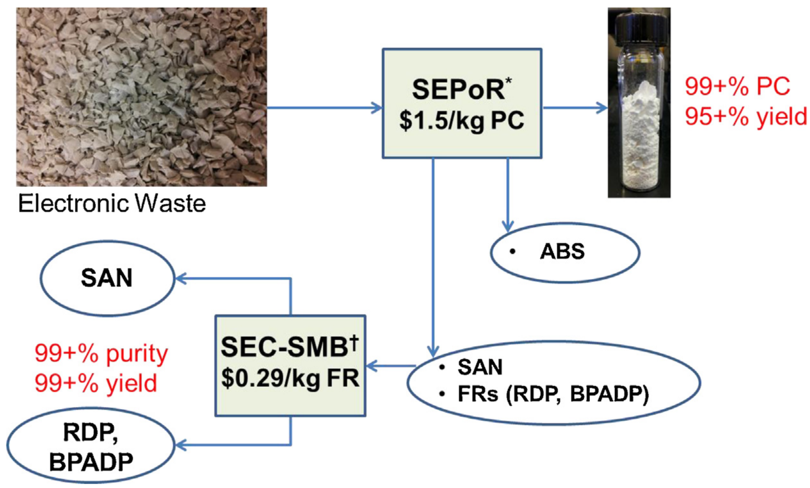


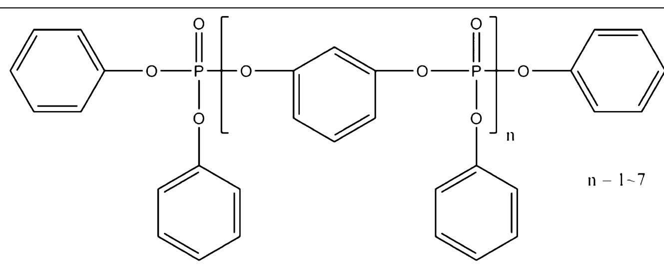
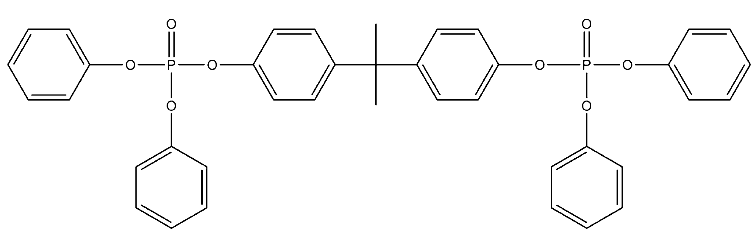
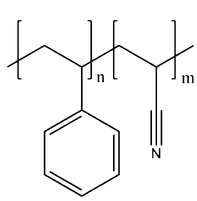
Fig. 1. Overview of Purdue process to recover high-purity polycarbonates and FRs from an electronic waste stream. *SEPoR process and cost estimate described in Weeden et al. [15]. †Cost estimate for 10,000 t FR/year, Table 7.

More than 500,000 t of FRs potentially could be recovered annually from WEEE. Furthermore, FRs must be removed for recovering high-purity polymers from wastes.

The existing literature on organophosphorus FRs in polymer wastes focuses on analytical methods for detection [20–23]. Microwave-assisted extraction, combined with gel permeation chromatography and mass spectrometry, was used to detect organophosphorus FRs in biological samples from fish and birds [24]. Solid phase extraction, combined with reverse phase chromatography, was used to detect FRs in water samples [25]. Pressurized liquid extraction (acetonitrile and water), combined with gas chromatography, was used to analyze sediment samples [26]. No literature has been found for recovering organophosphorus FRs from polymer waste at large scale.

Since the MW of the FRs and SAN differ by two orders of magnitude, size-exclusion chromatography (SEC) is a potential separation technique. SEC has been widely used for analyzing polymer mixtures [27,28]. SEC is a batch chromatography process, which is less efficient than simulated moving-bed (SMB) chromatography for large-scale production. SMB can achieve high product purity

Table 1
Main components of one of the side streams from the SEPoR process.

Component	Molecular structure	MW range (g/mol)	Bulk retail price ($/kg)[a]
RDP[b]		575–4025	4.00
BPADP[c]		693	3.00
SAN[d]		50,000–150,000	1.00

[a] Obtained from alibaba.com, May 2014.
[b] Resorcinol bis-diphenylphosphate.
[c] Bisphenol A bis-diphenylphosphate.
[d] Poly(styrene-co-acrylonitrile).