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Efficient Internal Plasticization of Poly(Vinyl Chloride) via Free Radical Copolymerization of Vinyl Chloride with an Acrylate Bearing a Triazole Phthalate Mimic

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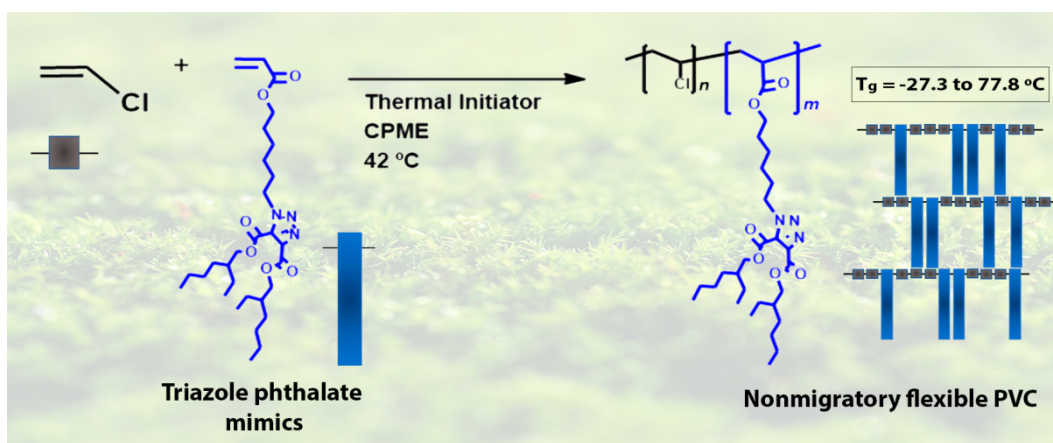
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Keywords: nonmigratory internal plasticization, poly(vinyl chloride), vinyl chloride, acrylate triazole phthalate mimics, free radical polymerization

Abstract

Nonmigratory internal plasticization of poly(vinyl chloride) (PVC) is achieved by synthesis of poly(vinyl chloride)-*co*-poly(4,5-bis(2-ethylhexyl)-1-[6-prop-2-enoyloxy]hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate [PVC-*co*-P(DEHT-HA)] copolymers via free radical polymerization (FRP). Optimization of the polymerization temperature, solvent, initiator, and vinyl chloride / acrylate (VC/DEHT-HA) monomer ratio were systematically investigated, and the corresponding glass transition temperatures (T_g) of the resultant copolymers determined. These internally plasticized copolymers were characterized by ^1H NMR, FTIR, SEC and DMTA. The T_g values of the PVC-*co*-P(DEHT-HA) copolymers range from -27 to 78 °C, and the physical properties suggest that the P(DEHT-HA) and PVC segments are miscible. Thermogravimetric analysis shows that increasing the ratio of the monomer DEHT-HA to vinyl chloride increases the thermal stability. By varying the initial VC/DEHT-HA monomer ratio, one can tune the T_g of the resulting copolymer, making both the strategy and the polymer flexible.

Graphical Abstract



1. Introduction

Poly(vinyl chloride) (PVC) is one of the most utilized polymers, due to its high versatility and low cost [1]. Applications in consumer products range from packaging to construction materials to health care devices [2, 3]. Pure PVC is a brittle and rigid solid, but its properties can be manipulated, ranging from rigid to extremely flexible, making it one of the most versatile of thermoplastic polymers [4-6]. With a glass transition temperature (T_g) around 100 °C, PVC requires the addition of plasticizers to become flexible, making it amenable to a variety of molding processes [7]. Most plasticizers used by the PVC industry are external, in that they are mixed into the PVC matrix. The most common class of external plasticizers are phthalate esters [8]; the most widely used is di(2-ethylhexyl)phthalate (DEHP, also known as DOP). Extensive studies have shown that phthalates leach out into the environment or evaporate into the atmosphere [9-13]. Legislative regulations increasingly ban or limit the use of DEHP and other phthalates. Phthalate migration [14, 15] results in serious negative effects on both human health and the environment, as well as the eventual deterioration of mechanical properties of PVC products [8, 14-17].

To achieve complete inhibition of plasticizer migration from PVC, covalent attachment of the plasticizer to the polymer backbone is an attractive strategy. Modification of PVC by displacement of some of the chlorine atoms has been demonstrated with several types of nucleophiles. Thiol plasticizers di(2-ethylhexyl) 4-mercaptophthalate (DEHP-SH), and di(2-ethylhexyl) 5-mercapto isophthalate (*iso*DEHP-SH) [14] have been explored. Use of azide nucleophile followed by thermal azide/alkyne cycloaddition has been used to prepare triazole phthalate-mimics such as di(2-ethylhexyl)-1H-triazole-4,5 dicarboxylate (DEHT), [18] as well as triazoles bearing pendant ether or esters attached

to di(2-ethylhexyl) phthalates [4]. Very recently, use of single poly(ethylene oxide) (PEO) ester triazoles [19] has demonstrated impressive plasticization. Post-polymerization attachment of plasticizers to PVC chains is sometimes problematic. Issues range from residual copper contamination when Cu-mediated azide/alkyne cycloaddition (CuAAC) is employed [4, 20-23], to partial dehydrochlorination of the PVC chain in the presence of amines acting as a base, resulting in low thermal stability [24].

Recent developments in Reversible Deactivation Radical Polymerization (RDRP) [2] provides the opportunity to prepare novel PVC-based materials previously unattainable by classical Free Radical Polymerization (FRP). For example, internal plasticization of PVC with control over the composition and molecular weight of the block copolymer of poly(vinyl chloride)-*b*-poly(*n*-butyl acrylate)-*b*-poly(vinyl chloride) (PVC-*b*-PBA-*b*-PVC) using single electron transfer degenerative chain transfer living radical polymerization (SET-DTLRP) [25, 26] was demonstrated. These materials have the same thermal and mechanical performance as commercial PVC using external phthalate plasticizers [7]. However, several adjustments are needed for industrial application: specifically the use of less expensive compounds (e.g. halogen based initiators, catalyst) and faster polymerization rates [27-32]. At this time, traditional FRP is the only affordable method for the synthesis of PVC at an industrial scale [2, 33].

In the present work, we investigate the preparation of various compositions of PVC-*co*-P(4,5-bis(2-ethylhexyl)-1-[6-prop-2-enoyloxy]hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate) [PVC-*co*-P(DEHT-HA)] copolymers by FRP (Scheme 1), with the aim of developing an industrially-viable nonmigratory flexible PVC. We envisioned the facile synthesis of an acrylate derivative bearing a phthalate-like side group, based on the very high plasticization efficiency of DEHP [5, 14, 15, 34].

chloride (Alfa Aesar, 96%, or $\geq 97\%$, 400 ppm phenothiazine stabilizer from Sigma Aldrich)), triethylamine (Acros, 99%) were used as received.

2.2. Characterization Techniques

400 MHz ^1H NMR spectra of samples were recorded on a Bruker Avance III 400 MHz spectrometer, with a 5 mm TIX triple resonance detection probe, in d_8 -THF with tetramethylsilane (TMS) as an internal standard. 500 MHz ^1H and ^{13}C spectra were recorded on a Bruker Avance III HD 4 channel Oxford Magnet NMR Spectrometer in CDCl_3 as solvent and internal standard. The chromatographic parameters of the samples were determined using a size exclusion chromatography set-up from Viscotek (Viscotek TDAmix) equipped with a differential viscometer (DV) and right-angle laser-light scattering (RALLS, Viscotek), low-angle laser-light scattering (LALLS, Viscotek) and refractive index (RI) detectors. The column set consisted of a PL 10 mm guard column ($50 \times 7.5 \text{ mm}^2$) followed by one Viscotek T2000 column (6 μm), one Viscotek T3000 column (6 μm) and one Viscotek LT4000L column (7 μm). A dual piston pump was set with a flow rate of 1 mL/min. The eluent (THF) was previously filtered through a 0.2 μm filter. The system was also equipped with an on-line degasser. The tests were done at 30 $^\circ\text{C}$ using an Elder CH-150 heater. Before the injection (100 μL), the samples were filtered through a polytetrafluoroethylene (PTFE) membrane with 0.2 μm pore. The system was calibrated with narrow PS standards. The dn/dc value was determined as 0.105 for PVC. Molecular weight (M_n^{SEC}) and dispersity ($D = M_w/M_n$) of synthesized polymers were determined by triple detection calibration using the OmniSEC software version: 4.6.1.354.

The Dynamic Mechanical Thermal Analysis (DMTA) of the samples was conducted in a Tritec2000DMA. The samples were placed in stainless steel material pockets and

analyzed in single cantilever mode. The tests were carried out in a temperature range from -120 °C to 120 °C, with a heating rate of 2°C.min⁻¹, in multifrequency mode (1, 10 Hz). The T_g was determined from the peak of tan δ curve, at 1Hz [35].

Fourier transform infrared (FTIR) spectra were obtained in the 4000–600 cm⁻¹ range at room temperature using an Agilent Technologies Cary 630 spectrometer, equipped with a Golden Gate single reflection diamond ATR. Data collection was performed with 4 cm⁻¹ spectral resolution and 64 accumulations.

The thermal stability of the samples was investigated by thermogravimetric analysis (TGA) using a STA 449 F3 Jupiter instrument. With a rate of 10°C/min the analysis was made between 25° and 600°C under nitrogen atmosphere.

The thermal behavior of the samples was further studied by differential scanning calorimetry (DSC) using a DSC 214 Polyma equipped with an Intracooler 40 cooling unit. The samples heated from 25 °C to 120 °C, at 10 °C/min, and then cooled to -40 °C. Then, they were heated again at 10°C/min from -40°C to 120°C. In the case of the P(DEHT-HA) homopolymer, the maximum temperature was set in 80 °C.

2.3. Procedures

Warning on Organic Azides: Organic azides can be dangerous in nature: low molecular weight organic azides have a propensity to violently decompose. A formula to determine if an organic azide is safe to handle has been suggested: $(N_{\text{Carbon}} + N_{\text{Oxygen}})/N_{\text{Azide Nitrogen}} \geq 3$, where N = number of atoms [36]. While 6-azidohexanol did not show signs of violent decomposition, extreme caution should be taken at all times when synthesizing or handling organic azides.

Synthesis of 4,5-bis(2-ethylhexyl)-1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate “DEHT-OH”

4,5-Bis(2-ethylhexyl)-1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate and 6-azidohexan-1-ol were synthesized as described previously [19]. 6-Azidohexan-1-ol (1.570 g, 10.98 mmol) was added to a 100 mL round-bottom flask with 35 mL of CHCl_3 . To this was added 1,4-bis(2-ethylhexyl) but-2-ynedioate (4.830 g, 14.27 mmol) and stirred at 50 °C for 24 h. The volatiles were evaporated under vacuum, affording a colorless crude oil. Purification via flash chromatography using 7:3 hexanes:ethyl acetate afforded 5.264 g (10.93 mmol, 99.53% yield) of a colorless oil, as a mixture of two diastereomers.

TLC SiO_2 : 7:3 hexanes:ethyl acetate, R_f =0.29, UV, *p*-anisaldehyde stain.

^1H NMR (500 MHz, CDCl_3): δ 4.58 (t, $J=7.3$ Hz, 2H), 4.33– 4.22 (m, 4H), 3.63 (t, $J=6.5$ Hz, 2H), 1.91 (p, $J=7.5$ Hz, 2H), 1.77– 1.64 (m, 2H), 1.55 (p, $J=6.6$ Hz, 2H), 1.44–1.26 (m, 21H), 0.97– 0.80 (m, 12H).

^{13}C NMR (125 MHz, CDCl_3 , DEPT): δ 160.5 (C=O), 158.8 (C=O), 140.4 (4°), 129.7 (4°), 69.1 (CH_2), 68.3 (CH_2), 62.5 (CH_2), 50.4 (CH_2), 38.7 (CH), 38.7 (CH), 32.4 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 26.1 (CH_2), 25.1 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.9 (CH_2), 14.0 (CH_3), 10.9 (CH_3).

IR (Neat): 3436 (s, OH), 2959 (s, alkane CH), 2932 (s, alkane CH), 2861 (s, alkane CH), 1733 (s, ester C=O), 1466 (s, methylene bending CH_2) cm^{-1} .

HRMS: Calcd. for $\text{C}_{26}\text{H}_{47}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 482.3588; Found 482.3588.

Preparation of 4,5-bis(2-ethylhexyl)-1-[6-prop-2-enoyloxy)hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate “DEHT-HA”

In a 250 mL round bottom flask was put 4,5-bis(2-ethylhexyl)-1-[6-hydroxyhexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (DEHT-OH) (9.740 g, 20.22 mmol) and triethylamine (3.0692 g, 30.33 mmol) in 50 mL of anhydrous THF and stirred. This mixture was cooled to 0 °C under N₂ for 15 min. Acryloyl chloride (5.4906 g, 60.66 mmol) diluted with 20 mL of anhydrous THF was added slowly *via* syringe over 15 min and allowed to stir at 0 °C for 1 hour, then at room temperature for an additional hour. The reaction mixture was concentrated *in vacuo* and diluted with 80 mL of ethyl acetate, then washed twice with 10 mL of 10% aqueous HCl. The organic layer was dried with NaSO₄ and filtered, then evaporated under vacuum, affording a crude orange oil. Purification via flash chromatography using 7:3 hexanes:ethyl acetate furnished the product (4.680 g, 8.735 mmol, 43.2% yield) as a clear oil, as a mixture of two diastereomers.

TLC SiO₂: 7:3 hexanes:ethyl acetate, R_f=0.71, UV, KMnO₄ and *p*-anisaldehyde stain.

IR (Neat): 32959 (s, alkane CH), 2932 (s, alkane CH), 2861 (s, alkane CH), 1738 (s, ester C=O), 1731 (s, ester C=O), 1463 (s, methylene bending CH₂), 1271 (s, ester stretch C-O), 1195 (s, ester stretch C-O), 985 (s, mono. sub. alkene bending C=C), 811 (s, mono. sub. alkene bending C=C) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 6.41 (d, *J*=17.2 Hz, 1H), 6.13 (dd, *J*=17.2, 10.8 Hz, 1H), 5.84 (d, *J*=10.8 Hz, 1H), 4.60 (t, *J*=7.3 Hz, 2H), 4.29 (m, 4H), 4.16 (t, *J*=6.5 Hz, 2H), 1.94 (m, 2H), 1.79–1.64 (m, 4H), 1.51–1.28 (m, 20H), 0.98–0.87 (m, 12H).

¹³C-NMR (125 MHz, CDCl₃, DEPT): δ 166.2 (Acrylate C=O), 160.6 (C=O), 158.9 (C=O), 140.5 (4°), 130.6 (CH₂ alkene), 129.6 (4°), 128.5 (CH alkene), 69.1 (CH₂), 68.4 (CH₂), 64.3 (O-CH₂ acrylate), 50.4 (CH₂), 38.73 (CH), 38.70 (CH), 30.21 (CH₂), 30.17 (CH₂), 30.1 (CH₂), 28.89 (CH₂), 28.86 (CH₂), 28.4 (CH₂), 26.1 (CH₂), 25.4 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 22.96 (CH₂), 22.94 (CH₂), 14.0 (CH₃), 10.9 (CH₃).

HRMS: Calcd. for C₂₉H₄₉N₃O₆ [M+H]⁺ 536.3694; Found 536.3686.

Typical procedure for the FRP of VC and DEHT-HA in CPME at 42 °C with [VC]₀/[DEHT-HA]₀ (% m/m) = 75/25

A 15-mL Ace Glass 8645#15 pressure tube equipped with a bushing and a plunger valve was charged with a mixture of DEHT-triazole-hexyl acrylate (400 mg, 0.7 mmol), AIBN (7.43 mg, 0.045 mmol), Trigonox 187 W40 (18.2 mg, 0.04 mmol) and CPME (2.4 mL) (previously bubbled with nitrogen for 10 min). Pre-condensed VC (1.2 mL, 17.5 mmol) was added to the tube. The exact amount of VC was determined gravimetrically. The tube was sealed, submerged in liquid nitrogen and degassed through the plunger valve by applying reduced pressure and filling the tube with nitrogen over 20 cycles. The valve was closed and the tube reactor was placed in a water bath at 42 °C ± 0.5 °C under stirring (800 rpm). After 22 h, the reaction was stopped. The tube was slowly opened, the excess VC was allowed to evaporate inside a fume hood, and the mixture was precipitated into methanol. The polymer was separated by filtration and dried in a vacuum oven until constant weight.

Typical procedure for the FRP of DEHT-HA in CPME at 42 °C

A 15-mL Ace Glass 8645#15 pressure tube equipped with a bushing and a plunger valve was charged with a mixture of DEHT-triazole-hexyl acrylate (800 mg, 1.4 mmol), AIBN (9.1 mg, 0.055 mmol), Trigonox 187 W40 (3.7 mg, 0.008 mmol) and CPME (1.2 mL) (previously bubbled with nitrogen for 10 min). The tube was sealed, submerged in liquid nitrogen and degassed through the plunger valve by applying reduced pressure and filling the tube with nitrogen over 20 cycles. The valve was closed and the tube reactor was placed in a water bath at 42 °C ± 0.5 °C under stirring (800 rpm). After 22 h, the reaction was stopped. The tube was slowly opened, the excess VC was evaporated

inside a fume hood, and the mixture was precipitated into methanol. The polymer was separated by decantation and dried in a vacuum oven until constant weight.

Typical procedure for the FRP of VC in CPME at 42 °C

A 50-mL Ace Glass 8645#15 pressure tube equipped with a bushing and a plunger valve was charged with a mixture of AIBN (23.2 mg, 0.14 mmol), Trigonox 187 W40 (56.9 mg, 0.13 mmol) and CPME (7.5 mL) (previously bubbled with nitrogen for 10 min). Pre-condensed VC (5 mL, 73 mmol) was added to the tube. The exact amount of VC was determined gravimetrically. The tube was sealed, submerged in liquid nitrogen and degassed through the plunger valve by applying reduced pressure and filling the tube with nitrogen over 20 cycles. The valve was closed and the tube reactor was placed in a water bath at 42 °C ± 0.5 °C under stirring (800 rpm). After 22 h, the reaction was stopped. The tube was slowly opened, the excess VC was allowed to evaporate inside a fume hood, and the mixture was precipitated into methanol. The polymer was separated by decantation and dried in a vacuum oven until constant weight.

Migration resistance test of the PVC-*co*-P(DEHT-HA)

The migration stability was determined by analyzing the amount of plasticizer that leaches out from the PVC into the liquid phase, following previous procedures [37-39]. The leaching test was carried out according to ASTM D 1239-98 [40, 41]. About 1g of the sample was dissolved in THF and the solution was deposited on a Petri dish and dried to afford a film. A 60 mm x 60 mm x 2 mm (~ 1 g) piece of PVC-*co*-P(DEHT-HA) copolymer was immersed in 50 mL of *n*-hexane (extraction solvent) at 25 °C. After 24 h, the solvent-extracted PVC sample was rinsed, and dried under the test conditions in a vacuum oven at 30 °C for 24 h.

3. Results and Discussion

3.1. Synthesis of 4,5-bis(2-ethylhexyl)-1-[6-prop-2-enoyloxy]hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (DEHT-HA)

One of the most efficient and common plasticizers used to prepare commercial flexible PVC is DEHP (also known as dioctyl phthalate “DOP”) [42]. Recent success in attaching DEHT (DiEthyl Hexyl Triazole, a mimic of DEHP) to PVC [18] as an internal plasticizer was the main inspiration for this project. Thus, a novel acrylate functionalized with a phthalate mimic was synthesized: DiEthyl Hexyl Triazole - Hexyl Acrylate (DEHT-HA), containing a flexible hexyl tether to the triazole ring (Fig. S1). First, 4,5-bis(2-ethylhexyl)-1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (DEHT-OH) was synthesized (Fig. S2) according to our previously described procedure [19].

The ^1H NMR spectrum of DEHT-HA is shown in Fig. S1. The assignment of proton resonances for DEHT-HA correspond to the following groups: vinyl $\text{CH}_2=\text{CH}-$, **a** at 5.8-6.4 ppm; $-\text{CH}_2-$ triazole, **b** at 4.5-4.6 ppm, $\text{O}-\text{CH}_2-$ **c** at 4.2-4.3 ppm, $\text{O}-\text{CH}_2-$, **d** at 4.1-4.15 ppm, alkyl groups **f** at 1.5-1.75 ppm and **g** at 1.2-1.45 ppm; $-\text{CH}_3$, **h** (0.8-0.95 ppm); and $-\text{CH}$ groups, **e** (1.95-1.75 ppm).

3.2. Synthesis and Characterization of PVC-*co*-P(DEHT-HA)

Following the successful preparation of DEHT-HA, a preliminary FRP random copolymerization experiment with VC and DEHT-HA was conducted using a

VC/DEHT-HA ratio of 75/25 (because acrylates are more reactive than VC), using a mixture of Trigonox 187 W40 and AIBN as the radical initiators (Trigonox/AIBN = 0.5%/0.5%), and CPME as a solvent (Monomer/Solvent, M/S = 1/1.5) at 42 °C (Table 1, entry 3). As expected, the conversion of VC (60.5%) was lower than the conversion of DEHT-HA (99.5%). The purified PVC-*co*-P(DEHT-HA) copolymer was submitted to ¹H NMR, FTIR and DMTA analyses.

The ¹H NMR spectrum of the random PVC-*co*-P(DEHT-HA) copolymer (Fig. S3) displays the expected signals obtained for polymerization of DEHT-HA and VC. The proton resonances for the hexyl-triazole side-chains DEHT-(CH₂)₆- (e, f, g, h, i, j, k) are similar to those of the monomer (Fig. S1), and the broad peaks c and d are characteristic of the poly(acrylate) backbone: -CH₂-CH(COO-R)-. The resonances of the repeat unit of PVC CH₂-CHCl: a (1.9–2.7 ppm) and b (4.2–4.7 ppm) are seen as expected. Using integration of methyl peaks k and the integrative sum of peaks b + e + f + g leads to a calculated value of 75 % PVC in the random PVC-*co*-P(DEHT-HA) copolymer (Table 1, entry 3).

The random PVC-*co*-P(DEHT-HA) copolymer was also analyzed by FTIR over the wavelength range of 4000-650 cm⁻¹ (Fig. S4). The FTIR spectrum of the PVC-*co*-P(DEHT-HA) copolymer shows characteristic absorption peaks of the two constituent polymers: 3000-2900 cm⁻¹ (C-H stretching vibration), 1725 cm⁻¹ (C=O of ester group of P(DEHT-HA)), 1547 cm⁻¹ (triazole, C=N, of P(DEHT-HA)), 1439 cm⁻¹ (δ CH₂ of PVC), 1252 cm⁻¹ (δ CH of PVC), 1193 cm⁻¹ (ν C-O of P(DEHT-HA)), 952 cm⁻¹ (ν CH₂ of PVC), and 691 cm⁻¹ (ν C-Cl of PVC) [43, 44].

Preliminary thermal characterization was carried out by DMTA to identify the glass transition temperature (T_g) of the PVC-*co*-P(DEHT-HA) copolymers. The DMTA

traces reveal $\text{Tan } \delta$ peaks that are sensitive to the frequency of measurement. The T_g corresponds to the maximum temperature of $\text{Tan } \delta$ at 1 Hz. A single $T_g = 46.8 \text{ }^\circ\text{C}$ was obtained for the PVC-*co*-P(DEHT-HA) copolymer (Table 1, entry 3) with 75 % of PVC (Fig. 1). The reduction in T_g of typical PVC (around $100 \text{ }^\circ\text{C}$) to $46.8 \text{ }^\circ\text{C}$ confirmed the plasticization effect of DEHT-HA. The single T_g also suggest that at least for this copolymer composition, the P(DEHT-HA) and PVC segments are fully miscible.

For comparative purposes, both PVC and P(DEHT-HA) homopolymers were synthesized using the same conditions (Table 1, entries 1 and 2). These homopolymers were analyzed by DMTA to determine T_g values. Fig. 1 clearly shows the T_g of the PVC-*co*-P(DEHT-HA) copolymer is observed between the T_g values of PVC ($108.7 \text{ }^\circ\text{C}$) and P(DEHT-HA) ($-44.4 \text{ }^\circ\text{C}$) homopolymers. The expected T_g for a PVC-*co*-P(DEHT-HA) copolymer with 75 % of PVC was determined by the Fox equation: $1/T_{g\text{FOX}} = x_{\text{PVC}}/T_{g\text{PVC}} + x_{\text{P(DEHT-HA)}}/T_{g\text{P(DEHT-HA)}}$. Thus, the experimental T_g value of $46.8 \text{ }^\circ\text{C}$ obtained for PVC-*co*-P(DEHT-HA) copolymer is even lower than the expected $T_{g\text{FOX}} = 54.6 \text{ }^\circ\text{C}$, indicating more effective plasticization of PVC than expected.

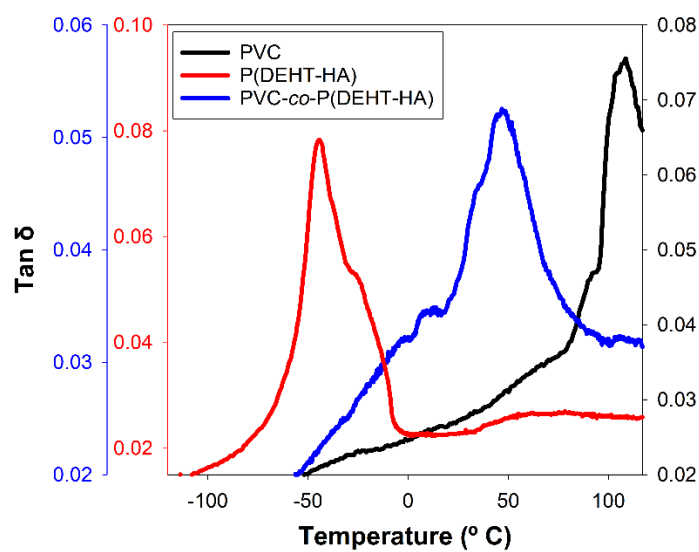


Fig. 1. $\tan \delta$ of PVC-co-P(DEHT-HA) copolymer (Table 1, entry 3) (blue line), PVC homopolymer (Table 1, entry 1) (black line) and P(DEHT-HA) homopolymer (Table 1, entry 2) (red line) at 1 Hz.

Thermogravimetric analysis of the PVC, P(DEHT-HA) and PVC-co-P(DEHT-HA) samples was carried out to infer their thermal stabilities. **Fig. 2** presents the weight loss curves of the samples in a nitrogen atmosphere over a 25 - 600 °C temperature range. The temperatures of interest taken from the thermogravimetric analysis are summarized in Table 1.

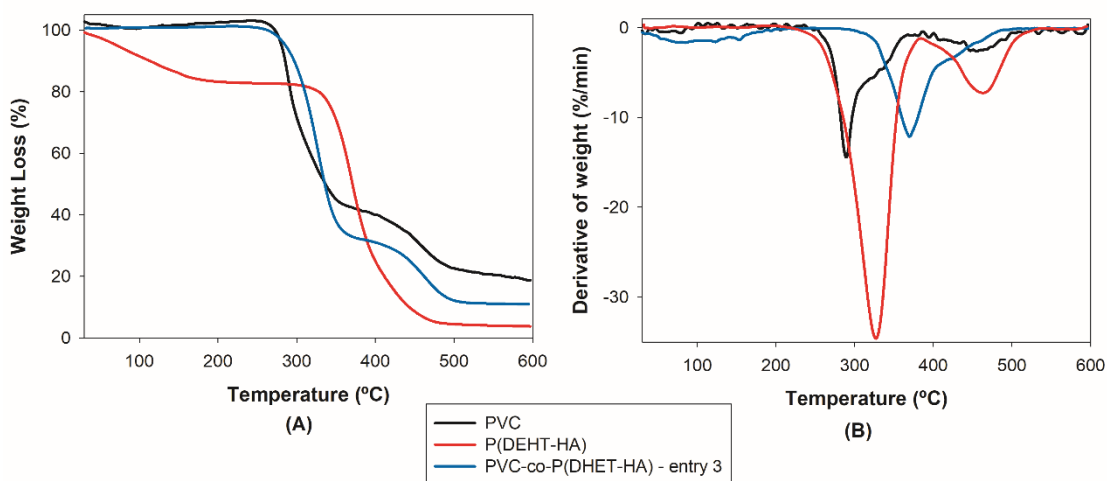


Fig. 2. Thermogravimetric curves of PVC, P(DEHT-HA) and PVC-co-P(DEHT-HA): TG(A) and DTG (B).

The thermogravimetric curves of PVC present two well-defined weight losses, as expected [45]. The first stage, ascribed to dehydrochlorination, occurs in a 250 °C - 375 °C temperature range, and the temperature of maximum rate (T_{p1}) occurs at 290 °C. The mass loss of this stage is about 60 %, which is in good agreement with what is typically reported in the literature [45-47]. The second degradation stage occurs in a temperature range of 380 °C - 560 °C, having a maximum of degradation rate at 456 °C. This stage is

ascribed to the degradation of the non-volatile products that result from the dehydrochlorination process [45-47].

The P(DEHT-HA) has a major weight loss step over the range of 290 °C - 540 °C; with a maximum of degradation rate at 370 °C. The onset temperature degradation (T_{on}) at 344 °C is consistent with the degradation temperature of triazole rings bearing alkyl chains [48]. An initial weight loss between 25 °C - 150 °C is also observed, which may be ascribed to the evaporation of residual solvent used in the purification step.

The PVC-co-P(DEHT-HA) copolymer (Table 1, entry 3) shows a weight loss profile resembling that of PVC, with two distinct stages. Such behaviour may be because this copolymer contains a significantly higher mass percentage of PVC than of P(DEHT-HA). It should be stressed that this copolymer demonstrates a higher thermal stability than the PVC homopolymer, as evidenced by the increase in T_{on} and T_p values (Table 1).

The samples were analyzed by DSC in order to evaluate their thermal behavior before degradation. All samples have an amorphous nature; their heat flow curves do not reveal any thermal transitions ascribable to melting. The heat flow curves corresponding to the 2nd heating are shown in Fig. S5.

Table 1Conversion and Polymer Characteristics of a Variety of PVC-*co*-P(DEHT-HA) Copolymers.

Entry	VC/DEHT-HA (w/w)	Time (h)	Temp. (°C)	Initiator (%)	Solvent (M/S)	Conv.vc (%)	Conv.DEHT-HA (%)	M _{n,SEC} x 10 ⁻³	D	% (w/w) PVC ^b	T _g (°C) : DMTA ^c	T _g (°C): Fox eq. ^d	T _g (°C): DSC ^e	T _{on1} (°C) ^f	T _{on2} (°C) ^f	T _{p1} (°C) ^g	T _{p2} (°C) ^g
1	100/0	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	56.5	--	25.08	1.95	100	108.7	--	76.3	276.1	426.6	289.3	455.1
2	0/100	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	--	99.5	40.40	2.30	--	-44.4	--	--	343.5	--	369.8 (446.1)*	--
3	75/25	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	60.5	99.5	22.52	1.85	75.4	46.8	54.6	36.6	294.7	430.9	327.0	463.3
4	75/25	22	42	1 (Trigonox)	CPME (1/1.5)	49.7	99.5	11.02	2.14	64.2	49.6	34.9	21.0	293.1	430.6	325.7	463.6
5	75/25	22	42	1 (AIBN)	CPME (1/1.5)	68.1	99.5	9.47	1.96	72.7	50.0	49.7	30.2	286.0	438.4	320.1	460.1
6	75/25	22	42	1 (0,5 Trigonox + 0,5 AiBN)	DMSO (1/1.5)	32.1	92.9	17.56	2.16	64.0	34.8	34.5	29.3	275.9	436.1	313.2	445.8
7	75/25	22	60	1 (0,5 Trigonox + 0,5 AiBN)	DMSO (1/1.5)	61.2	95.8	19.16	2.06	68.5	47.9	42.2	32.1	264.2	427.1	293.1	455.8
8	90/10	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	65.8	99.5	19.63	1.95	87.8	77.8	79.8	63.3	292.0	443.4	331.8	480.4
9	50/50	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	35.0	91.7	27.71	2.10	34.2	0.4	-8.0	--	304.4	--	317.2 (365.8)*	459.5
10	25/75	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	77.0	86.7	42.04	2.23	15.9	-27.3	-28.8	--	336.4	--	367.2	470.8
11 ^a	0/100	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	--	97.2	19.63	2.33	--	-56.6	--	--	381.4	--	413.9	--
12 ^a	75/25	22	42	1 (0,5 Trigonox + 0,5 AiBN)	CPME (1/1.5)	76.4	98.9	16.27	2.02	65.2	*	28.6	--	265.2	415.0	286.3	455.1

^a Hexyl acrylate (HA) was used instead of DEHT-HA; ^b Determined by ¹H NMR analysis; ^c Determined by DMTA analysis; ^d Determined by Fox Equation: $1/T_{gFOX} = x_{PVC}/T_{gPVC} + x_{P(DEHT-HA)}/T_{gP(DEHT-HA)}$; ^e Determined by DSC; ^fT_{on}: onset temperature; determined by TGA, TG curve; ^gT_p: temperature at which the weight loss is maximum; determined by TGA, DTG curve.; * Presented more than one maximum temperature of Tan δ at 1 Hz; ^hShoulder in the DTG curve.

3.3. Influence of Polymerization Temperature

Temperature is an important parameter to consider when optimizing polymerization conditions. The choice of temperature becomes even more important when using conventional thermal radical initiators (Trigonox and AIBN). Additionally, temperature is particularly crucial for the polymerization of VC, because high temperatures result in a higher concentration of structural defects in the PVC structure, with concomitant lower thermal stability [2]. Thus, a brief study of the influence of temperature on the polymerizations was carried out. FRP of VC and DEHT-HA was evaluated at 42 °C and 60 °C (Table 1, entries 6 and 7). Polymerization at 60 °C resulted in a slightly higher percent of VC content in the PVC-*co*-P(DEHT-HA) copolymer compared to polymerization at 42 °C. Consequently, carrying out the polymerization at 42 °C results in more incorporation of the monomer bearing the plasticizer mimic DEHT-HA, resulting in a lower T_g (34.8 °C) compared to the copolymer prepared at 60 °C (T_g = 47.9 °C). For polymerizations at both temperatures, the T_g values determined by DMTA are very similar to those predicted by the Fox equation.

Regarding the thermal stability, the copolymer synthesized at 42 °C (Table 1, entry 6) is thermally more stable than the copolymer obtained at 60 °C (Table 1, entry 7). A decrease of *ca.* 10 °C in the T_{on} values is observed for the PVC-*co*-P(DEHT-HA) copolymer synthesized at 60 °C compared to the copolymer synthesized at 42 °C. The thermogravimetric curves of both copolymers are shown in the Supporting Information (Fig. S6).

No other significant differences, particularly in M_n and D , were noted. Therefore, 42 °C was chosen as the polymerization temperature for the following studies.

3.4. Influence of the Solvent

After establishing the temperature, the influence of the solvent was addressed. Because PVC is very insoluble in its own monomer, as well as in most common organic solvents, DMSO [28, 30, 49-51] and cyclopentyl methyl ether (CPME) [27, 52, 53] were tested (Table 1, entries 3 and 6). While DMSO is a commonly utilized organic solvent for VC polymerization, CPME has emerged as a green alternative, due to its high hydrophobicity, relative stability under both acidic and basic conditions, and low tendency to form dangerous peroxide by-products [54]. Moreover, CPME demonstrates negative skin sensitization [55], presents no genotoxicity and no mutagenicity [56], and is approved by the *Toxic Substances Control Act* (TSCA) and the *European List of Notified Chemical Substances* (ELINCS) [52-54]. Under similar polymerization conditions, CPME (Table 1, entry 3) gave higher conversions for both monomers VC and DEHT-HA. With respect to *D*, DMSO performed better (Table 1, entry 6). The experimental T_g obtained using CPME was even lower than the T_{gFOX} , indicating more effective plasticization of PVC compared to that when DMSO was used as the solvent.

In terms of the thermal stability (Table 1, entries 3 and 6), both PVC-*co*-P(DEHT-HA) copolymers prepared with DMSO or CPME have similar T_{on} , and thus similar thermal stability. The thermogravimetric curves are shown in supporting information (Fig. S7).

Given these results and the “green” properties [52, 53] of CPME, the ether was selected as the preferred solvent for this study.

3.5. Influence of the Thermal Initiator

In the copolymerizations studied to this point, a mixture of the two thermal initiators (0.5%/0.5% to monomers) having very distinct half-lives were used to generate radicals: AIBN ($t_{1/2} = 1$ h at 82 °C) and Trigonox 187-W40 ($t_{1/2} = 1$ h at 39 °C) [57]. To study the influence of these initiators on the (co)polymerization of VC and DEHT-HA, these initiators were evaluated separately (1% to monomers) (Table 1, entries 3, 4 and 5). When only Trigonox was utilized, the conversion of VC was lower than when AIBN was used alone or as a mixture of AIBN and Trigonox. When the mixture of initiators was used, a narrower D for the PVC-*co*-P(DEHT-HA) copolymer was obtained. These results may be explained in that isopropyl radical (formed from decomposition of diisobutyl peroxide in Trigonox 187-W40: $(\text{CH}_3)_2\text{CH}-\text{C}(\text{O})-\text{O}-\text{O}-\text{C}(\text{O})-\text{CH}(\text{CH}_3)_2$) adds much faster to both VC [32] and DEHT-HA as compared to the somewhat stabilized isopropylcyano radical formed by AIBN thermal decomposition. The experimental T_g obtained using the mixture of initiators was even lower than the predicted $T_{g\text{FOX}}$, indicating more effective plasticization of PVC than when either initiator was used separately in the polymerization.

The thermal stabilities of the PVC-*co*-P(DEHT-HA) copolymers synthesized with different initiators were very similar, as inferred by the values of $T_{\text{on}1}$. The thermogravimetric curves are shown in Fig. S8.

Thus, a mixture of initiators Trigonox and AIBN were used for the rest of these studies.

3.6. Influence of VC/DEHT-HA Monomer Ratios

With the main objective to obtain different degrees of internal plasticization of PVC, four VC/DEHT-HA monomer ratios were investigated under the optimized conditions (CPME at 42 °C): 75/25, 90/10, 50/50 and 25/75 (Table 1, entries 3, 8, 9 and 10). Use

of higher ratios of DEHT-HA to VC resulted in higher P(DEHT-HA) incorporation in the PVC-*co*-P(DEHT-HA) copolymer, as expected. Fig. 3 clearly shows different T_g values, ranging between the T_g values of the homopolymers PVC (108.7 °C) and P(DEHT-HA) (-44.4 °C). Independent of copolymer composition, the P(DEHT-HA) and PVC segments are miscible. Thus, the different internal plasticization can be tuned by varying the P(DEHT-HA) content in the PVC-*co*-P(DEHT-HA) copolymer.

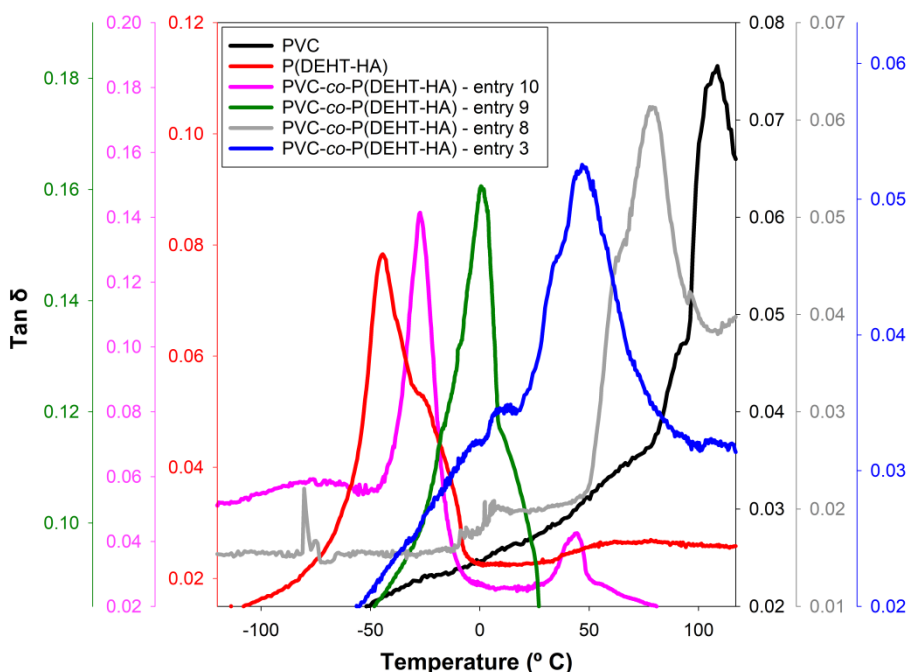


Fig. 3. Tan δ of PVC-*co*-P(DEHT-HA) copolymer (3:1 DEHT-HA : VC initial monomer ratio, Table 1, entry 10) (pink line), PVC-*co*-P(DEHT-HA) copolymer (1:1 DEHT-HA : VC initial monomer ratio, Table 1, entry 9) (green line), PVC-*co*-P(DEHT-HA) copolymer (1:3 DEHT-HA : VC initial monomer ratio, Table 1, entry 3) (blue line), PVC-*co*-P(DEHT-HA) copolymer (1:9 DEHT-HA : VC initial monomer ratio, Table 1, entry 8) (grey line), PVC homopolymer (Table 1, entry 1) (black line) and P(DEHT-HA) homopolymer (Table 1, entry 2) (red line) at 1 Hz.

Increasing the amount of DEHT-HA in these copolymers contributes to an increase in the thermal stability of the copolymers by TGA. For example, an increase of 44 °C in

the value of T_{on1} was observed when the amount of DEHT-HA went from 12 % (w/w) (entry 8) to 84 % (w/w) (entry 10). This makes sense, as P(DEHT-HA) has a superior thermal stability compared to PVC. Interestingly, the thermogravimetric curves of the copolymers with initial amounts of DEHT-HA of 66 % (w/w) (entry 9) and 84 % (w/w) (entry 10) resemble that of P(DEHT-HA) homopolymer, all of which display only one stage of weight loss. The thermogravimetric curves are presented in the Supporting Information (Fig. S9).

3.7. Influence of 2-EthylHexyl Triazole Phthalate-mimic Functionality

To probe the influence of the phthalate-like triazole diester group in the monomer DEHT-HA on internal plasticization of PVC, hexyl acrylate (HA) (similar to DEHT without the triazole group) was used to prepare a PVC-*co*-PHA copolymer (Table 1, entry 12, initial monomer ratio 75:25 VC:HA) and a PHA homopolymer (Table 1, entry 11). Comparing the copolymers made from 75:25 VC:HA (entry 12) to 75:25 VC:DEHT (entry 3) in Table 1, the conversions of the monomers and the macromolecular characteristics are very similar. However, it is not possible to identify a single T_g by DMTA for this new PVC-*co*-PHA copolymer (Fig. 4), whereas the analogous PVC-*co*-P(DEHT-HA) copolymers all give clear single T_g values. This suggests for this PVC-*co*-PHA copolymer, segments of PHA are immiscible with the PVC segments. Thus, the presence of the triazole diester phthalate mimic seems essential to obtain effective internal plasticization of PVC.

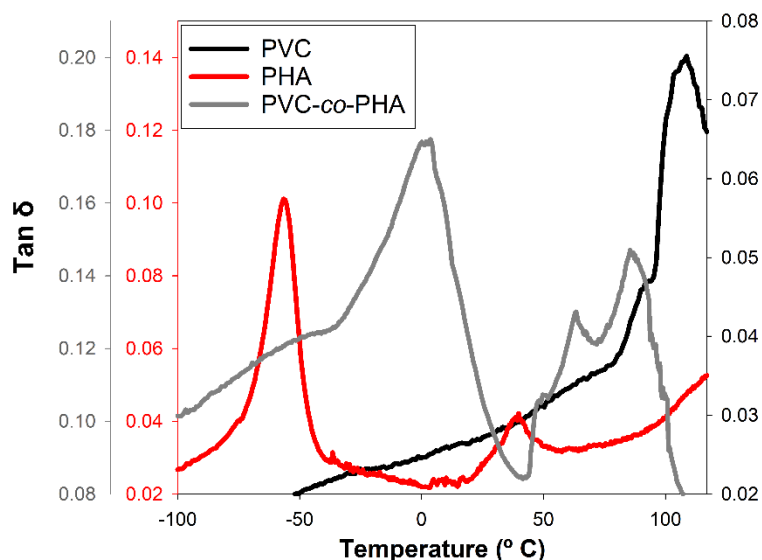


Fig. 4. $\tan \delta$ of PVC-*co*-PHA copolymer (3:1 VC:HA initial monomer ratio, Table 1, entry 12) (grey line), PVC homopolymer (Table 1, entry 1) (black line) and PHA homopolymer (Table 1, entry 11) (red line) at 1 Hz.

The thermogravimetric results show that both P(DEHT-HA) and PHA degrade in a single stage at temperatures higher to that observed for PVC (Fig. S10). The degradation profile of PHA gives a value of T_{on} of *ca.* 381 °C, ascribed to the degradation of the ester linkages [58, 59]. The PVC-*co*-P(DEHT-HA) displays a higher thermal stability than PVC-*co*-PHA. However, homopolymer P(DEHT-HA) has a lower thermal stability compared to homopolymer PHA. Overall, this suggests superior interaction of the triazole diester portions with PVC regions, in accordance with the DMTA results.

DSC analysis shows that the PHA homopolymer and PVC-*co*-PHA copolymer are amorphous, similar to that observed for the PVC-*co*-P(DEHT-HA) copolymers. The heat flow curves (2nd heating cycle) are shown in the Supporting Information (Fig. S5).

3.8. Migration Resistance of PVC-*co*-P(DEHT-HA)

When PVC is used for the production of baby bottles, food packaging, synthetic leather, and medical tubing, it is mandatory that there be no migration of the plasticizer out of the consumer product. Migration is determined by analyzing the amount of plasticizer that leaches out from the PVC sample into a liquid phase. The solvent *n*-hexane is commonly used as the extraction medium to test migration stability of plasticized PVC, as the solubility profile of *n*-hexane is similar to that of cooking oil [60, 61].

Thus PVC-*co*-P(DEHT-HA) copolymer with 75% PVC (Table 1, entry 3) was submitted to migration studies in *n*-hexane. The results show the weight loss of PVC-*co*-P(DEHT-HA) copolymer is almost negligible (% weight loss = $[(1.430 \text{ g} - 1.405 \text{ g})/1.430 \text{ g}] \times 100\% = 1.75 \%$) as compared with commercial formulations of PVC externally plasticized with DEHP (~41% for 100 phr DEHP and ~21% for 40 phr DEHP) [7, 26, 62]. Comparing T_g values by DMTA of the PVC-*co*-P(DEHT-HA) copolymer before (46.8 °C) and after (42.3 °C) extraction with *n*-hexane (Fig. 5) shows no significant difference. Moreover, there was no difference in molecular weight distribution of the pre- and post-extraction copolymers, as determined by SEC (Fig. 6).

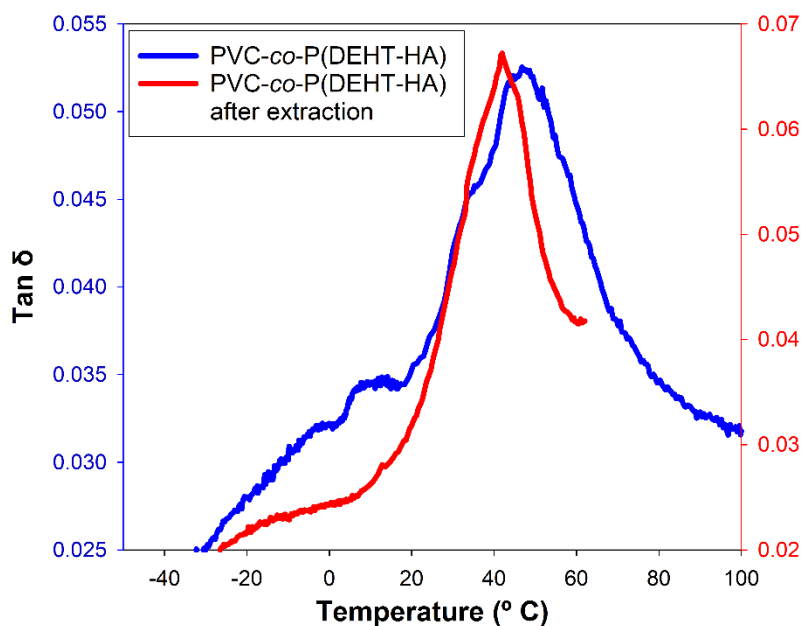


Fig. 5. Tan δ of PVC-*co*-P(DEHT-HA) with 75.4 % PVC (Table 1, entry 3) at 1 Hz, before (blue line) and after (red line) extraction with *n*-hexane.

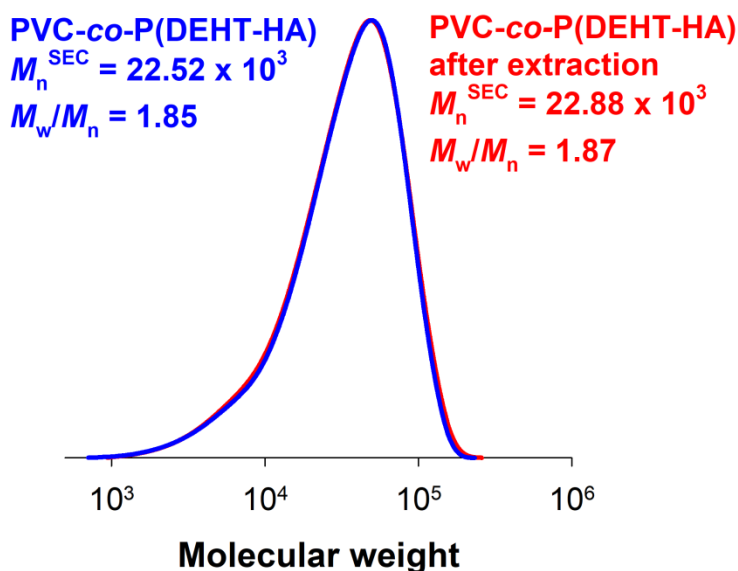


Fig. 6. SEC chromatograms of PVC-*co*-P(DEHT-HA) containing 75.4 % PVC (Table 1, entry 3), before (blue line) and after (red line) extraction with *n*-hexane.

Cumulatively, these results provide compelling evidence that the plasticizing moieties of PVC-*co*-P(DEHT-HA) copolymer are indeed covalently bonded to the polymer.

4. Conclusions

PVC-*co*-P(DEHT-HA) copolymers containing varying amounts of pendant triazole diesters were successfully synthesized via FRP to achieve nonmigratory internal plasticization of PVC. Careful optimization of reaction conditions (VC:DEHT-HA initial monomer ratios, choice of thermal initiator, choice of solvent, and polymerization temperature) provides a commercially viable system with the ability to fine tune the T_g of the PVC-*co*-P(DEHT-HA) copolymers. Structural analysis by ^1H NMR and FTIR,

SEC, and thermomechanical DMTA, DSC and TGA analysis were carried out to probe the PVC-*co*-P(DEHT-HA) copolymers. The single T_g values range from -27 °C to 78 °C, suggesting that P(DEHT-HA) and PVC segments are miscible. The inclusion of higher amounts of DHET-HA in the copolymer enhances the thermal stability.

As a control, removal of the pendant triazole diethylhexyl esters by using *n*-hexyl acrylate confirms that the triazole phthalate mimic is required for effective plasticization. Migration resistance by extraction studies with *n*-hexane, corroborated by thermogravimetric and SEC analysis of virgin and post-extraction copolymer, demonstrates that the plasticizing moieties are covalently bonded to PVC.

Declaration of competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Experimental data and results: ^1H , ^{13}C and DEPT NMR spectra of DEHT-OH and DEHT-HA, ^1H NMR spectrum of a PVC-*co*-P(DEHT-HA) copolymer, and DSC and T_g data of PVC-*co*-P(DEHT-HA) copolymers. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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