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Internal Plasticization of Poly(Vinyl Chloride) by Grafting Acrylate Copolymers via Copper-Mediated Atom Transfer Radical Polymerization

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((Additional Supporting Information may be found in the online version of this article.))

ABSTRACT

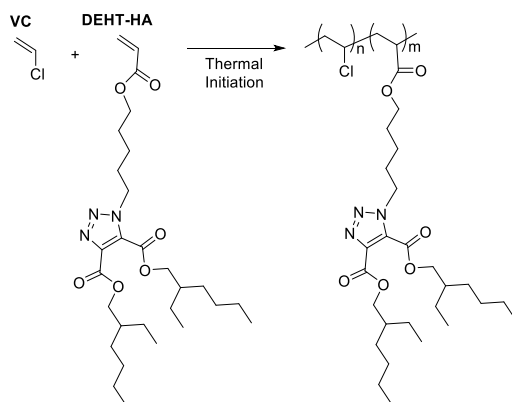
Internal plasticization of poly(vinyl chloride) (PVC) was achieved in one-step using copper-mediated atom transfer radical polymerization (ATRP) to graft different ratios of random *n*-butyl acrylate (BA) and 2-2-(2-ethoxyethoxy)ethyl acrylate (2EEA) copolymers from defect sites on the PVC chain. Five graft polymers were made with different ratios of poly(*n*-butyl ester) (PBA) and poly(2-2-(2-ethoxyethoxy)ethyl acrylate) (P2EEA); the glass transition temperatures (T_g) of functionalized PVC polymers range from -25 to -50 °C. Single T_g values were observed for all polymers, indicating good compatibility between PVC and grafted chains, with no evidence of microphase separation. Plasticization efficiency is higher for polyether P2EEA moieties compared with PBA components. The resultant PVC graft copolymers are thermally more stable compared to unmodified PVC. Increasing the reaction scale from 2 g to 14 g produces consistent and reproducible results, suggesting this method could be applicable on an industrial scale.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most popular thermoplastics, with applications ranging from toys, packing materials, medical devices, car dashboards to construction pipes.¹ Plasticizers are added to PVC to achieve desirable mechanical properties. In medical devices, for example, plasticizer content can be as high as 50 wt %.² Phthalates are the dominant PVC plasticizer in the global market, with di(2-ethylhexyl)phthalate (DEHP, also known as DOP) comprising up to 70% of the phthalates utilized. However, small molecules plasticizers can leach out from the PVC matrix, resulting in significant health problems for humans³ from inhalation and absorption, as well as in damage to the environment,⁴⁻⁹ with concomitant decay of mechanical properties of the materials over time.

The most efficient way to prevent leaching of plasticizers is to covalently attach them to PVC. This is referred to as “internal plasticization.” The flexibility of a polymer is indicated by its glass transition temperature (T_g), with lower T_g values observed for more flexible materials. Different nucleophilic substitution methods have been explored for chemically attaching plasticizers to PVC, including sulfide linkages,¹⁰⁻¹⁴ amine linkages,¹⁵⁻¹⁷ and triazole linkages.¹⁸⁻²⁷ All of these methods require three or more synthetic steps. The lowest T_g of -42 °C reported to date was achieved in three steps using 84 wt % of an attached plasticizer by the Braslau group.²⁶ Another strategy involves the formation of copolymers of vinyl chloride with other monomers. For example, PVC-*b*-poly(*n*-butyl acrylate) (PBA)-*b*-PVC was prepared by Coelho^{28,29} using a two-step process utilizing a single electron transfer – degenerative chain transfer living radical polymerization. In this case, the lowest T_g value obtained was -16 °C.²⁸ In 2020, Coelho and Braslau³⁰ prepared random copolymers of vinyl chloride (VC) with an acrylate bearing a triazole phthalate mimic (4,5-bis(2-ethylhexyl)-1-[6-prop-2-enoyloxy) hexyl]-1H-1,2,3-triazole-

4,5-dicarboxylate (DEHT-HA)) using free radical polymerization (**Scheme 1**). The lowest T_g value was $-27\text{ }^\circ\text{C}$ for a random copolymer containing 74 wt% of DEHT-HA. However, the preparation of monomer DEHT-HA required four synthetic steps. Thang, Moad and Feng³¹ prepared PVC-*b*-polycaprolactone (PCL) in a two-step polymerization process using reversible addition–fragmentation chain transfer (RAFT) polymerization, followed by ring-opening polymerization (ROP). T_g values as low as $-35\text{ }^\circ\text{C}$ were achieved using 90 wt % of PCL. The Z.-M. Li group synthesized flexible latex particles made of PBA/PVC-*g*-PBA through a multistage emulsion polymerization method. However, two T_g values were observed, indicating phase separated materials.³²



Scheme 1 Synthesis of PVC-*co*-P(DEHT-HA) to give internally plasticized material³⁰

Atom transfer radical polymerization (ATRP),^{33–35} a reversible–deactivation radical polymerization,³⁶ has been utilized to grow graft copolymers off of PVC chains. Matyjaszewski used PVC containing 1 mol % of randomly incorporated vinyl chloroacetate monomer as a macroinitiator to grow PVC-*g*-PBA.³⁷ The chlorine atoms on the vinyl chloroacetate residues function as initiation sites for ATRP. A T_g value of $-19\text{ }^\circ\text{C}$ was achieved with 65 mol % of PBA

grafts. Several research groups have utilized activated chlorines at PVC defect sites to prepare PVC-graft copolymers by ATRP.³⁸⁻⁴⁸ These defect sites include both allylic and tertiary chlorides (**Figure 1**).⁴⁹ Estimates of allylic chloride content ranges from 0.05-0.72/1000 vinyl chloride units,^{50,51} and tertiary chloride content from 0.7-2.1/1000 vinyl chloride units.⁵² Although these estimates vary, there is usually at least one defect site in each PVC chain.³⁸ Percec and Asgarzadeh³⁸ carried out a systematic study of Cu-catalyzed ATRP directly from defects sites on PVC, achieving functionalized PVC materials in a single step. The lowest T_g value obtained was -4 °C for PVC-*g*-PBA with 53 mol% of PBA grafts. Emre⁴¹ applied Cu-ATRP with 2-ethyl hexylacrylate as a DEHP mimic to grow grafts from PVC, obtaining a T_g value of 58 °C. These authors speculated that there are up to 4% of defect sites per PVC chain. Similarly, PVC-*g*-poly(oxyethylene methacrylate) (POEM) prepared by Ahn *et al.*⁴³ using Cu-catalyzed ATRP resulted in a material with two T_g values (-68 °C and 32 °C), indicating micro-phase separation.

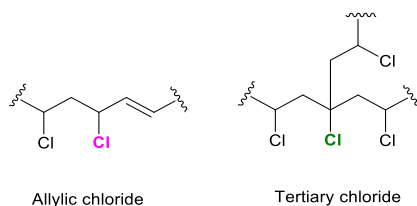
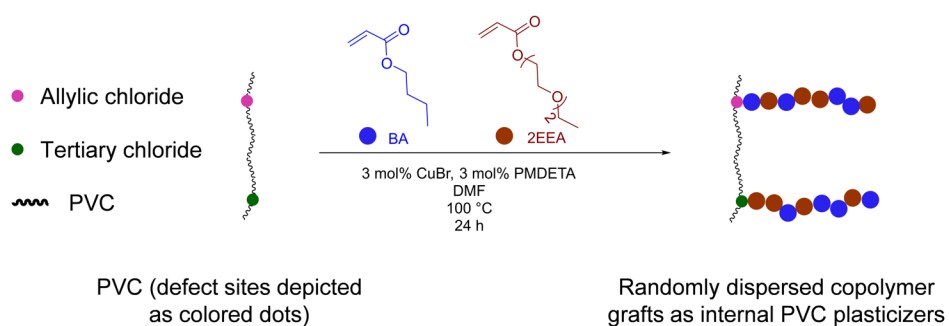


Figure 1 Structural defects of commercial PVC

Polyethers have been utilized by a number of researchers as highly effective internal plasticizers for PVC.^{13,14,26,27} Polyether chains tend to be more effective compared to analogous materials with straight-chain or branched alkyl groups. Multiple groups have demonstrated good compatibility between PVC and PBA segments in graft copolymers.^{37,38} In this paper, we investigated combining the compatibility of BA with the plasticizing efficiency of polyethers.

Although Cu-ATRP is generally more effective with methacrylates than acrylates, the rigidity imposed on the graft chains by the quaternary carbon bearing the methacrylate methyl group makes polyacrylates better plasticizers than polymethacrylates. Thus, graft polymerization of different ratios of poly(*n*-butyl acrylate)-*co*-poly(2-(2-ethoxyethoxy)ethyl acrylate) (PBA-*co*-P2EEA) were generated to achieve effective plasticization while avoiding microphase separation (Scheme 2).



Scheme 2 General Scheme: Preparation of PVC-*g*-PBA-*co*-P2EEA via ATRP

EXPERIMENTAL

Materials

PVC ($M_w = 43,000$, $M_n = 22,000$) was purchased from Sigma-Aldrich and was purified before use by the following method:²⁶ PVC (40.05 g, 640.8 mmol) was dissolved in 200 mL of tetrahydrofuran (THF). The polymer was precipitated by addition to 1 L of methanol (MeOH). The precipitate was filtered, dissolved in 230 mL of THF, and precipitated again in 1 L of MeOH. The precipitate was filtered, dissolved in 230 mL of THF, and finally precipitated in 2 L of MeOH. The precipitate was filtered and dried under vacuum. Copper bromide (CuBr) was purchased from Oakwood Chemical and was purified by the following method:⁵³ 7.08 g of CuBr was

suspended in 20 mL of glacial acetic acid, and stirred under nitrogen at room temperature overnight. The solid was filtered using a Büchner funnel, washed with 200 mL of absolute ethanol, followed by 100 mL of anhydrous diethyl ether. The solid CuBr was then dried under vacuum, and stored under N₂ at -20 °C. *n*-Butyl acrylate (BA) (>99%) was purchased from Acros Organics and purified to remove the inhibitor by distillation under reduced vacuum. 2-2-(2-ethoxyethoxy)ethyl acrylate (2EEA) (98%) was purchased from TCI America and purified to remove inhibitor by passing it neat through basic aluminum oxide. *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA) (99%) was purchased from Sigma-Aldrich and purified before use by distillation under reduced vacuum. Dimethylformamide (DMF) (extra dry, 99.8%) was purchased from Acros Organics. MeOH (99.8%), THF (99.9%), and acetic acid (99.7%) were purchased from Fisher Chemical. Basic aluminum oxide was purchased from Oakwood Chemical.

Measurements

Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AVANCE III HD 4 channel 500 MHz Oxford Magnet NMR Spectrometer with Automation at ambient temperature in CDCl₃ as solvent. The signal of residual CHCl₃ was used as an internal standard (¹H NMR, δ 7.26 ppm). Fourier transform infrared spectroscopy (FTIR) was recorded with a Thermo-Nicolet 6700 Fourier Transform Infrared spectrometer equipped with a Continuum microscope in transmission mode. A small portion of each sample was transferred to an infrared transmitting substrate. The analytical spot size was approximately 100 microns x 100 microns. OMNIC 8.0 software was used to perform data analysis. Glass transition temperatures of polymers were measured using TA Instruments DSC Q2000 with a heat-cool-heat protocol.

DSC was equilibrated at 180 °C. First heat cycle: a scanning range of –180 to 240 °C at a heating rate of 10 °C min⁻¹. First cool cycle: 240 °C to -175 °C at 5 °C min⁻¹. Second heat cycle: -175 °C to 240 °C at 10 °C min⁻¹. Derivative thermogravimetry (DTG) and thermal gravimetric analyses (TGA) were performed with TA Instrument TGA Q500. TGA was performed within a scanning range of ambient to 900 °C at a heating rate of 10 °C min⁻¹ with nitrogen purge. Gel Permeation Chromatography (GPC) was recorded with a Malvern Viscotek TDA 305 Triple Detector. Sample was dissolved in THF with concentration 1 mg/mL. The column set used was PLgel 50A. The flow rate was 1 mL/min. Injection volume was 100 µL.

Preparation of 14 g scale (Preparation of 2 g scale samples is provided in Supporting Information)

Preparation of PVC-g-PBA (14 g scale)

To a 50 mL Schlenk flask was added PVC (3.00 g, 48.0 mmol) and DMF (18 mL). The mixture was stirred and warmed slightly to fully dissolve the PVC. BA (17.2 mL, 120 mmol) was added to the solution. To a 20 mL vial was added CuBr (206.50 mg, 1.4395 mmol). 6 mL of DMF was used to transfer CuBr to the PVC solution by pipet. PMDETA (0.30 mL, 1.43 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C while stirring under nitrogen. After 24 h, an aliquot was taken to analyze the crude reaction by ¹H NMR using CDCl₃ as solvent (%conv._{NMR} = 87%). The resulting polymer was diluted in 20 mL of THF and precipitated by addition to 400 mL of MeOH. The polymer was washed with stirring with two additional portions of MeOH (400 mL × 2) and gently stirred in MeOH overnight. Then MeOH was decanted. The polymer was dissolved in 30 mL of THF and

then stirred in 400 mL of MeOH overnight. The polymer was washed with stirring with two additional portions of MeOH (400 mL \times 2). The polymer was filtered and dried under vacuum to yield 14.98 g (wt% plasticizer_{grav.} = 80%) of a pale green, pliable polymer.

¹H NMR (500 MHz, CDCl₃, δ): 4.65–4.54 (br m), 4.54–4.38 (br m), 4.38–4.23 (br m), 4.15–3.85 (br m), 2.50–2.22 (br m), 2.22–1.97 (br m), 1.97–1.79 (br m), 1.77–1.56 (br m), 1.51–1.43 (br m), 1.43–1.29 (br m), 0.94 (t, J = 7.3 Hz). Based by ¹H NMR integration: PBA : PVC = 1.4 : 1.0.

Preparation of PVC-g-75%PBA-co-25%P2EEA (14 g scale)

To a 50 mL Schlenk flask was added PVC (3.00 g, 48.0 mmol) and DMF (18 mL). The mixture was stirred and warmed slightly to fully dissolve the PVC. BA (12.9 mL, 90.0 mmol) and 2EEA (5.56 mL, 30.0 mmol) were added to the solution. To a 20 mL vial was added CuBr (206.36 mg, 1.4386 mmol). 6 mL of DMF was used to transfer CuBr to the PVC solution by pipet. PMDETA (0.30 mL, 1.43 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C while stirring under nitrogen. After 24 h, an aliquot was taken to analyze the crude reaction by ¹H NMR using CDCl₃ as solvent (%conv._{NMR} = 88%). The resulting polymer was diluted in 20 mL of THF and precipitated by addition to 400 mL of MeOH. The polymer was washed with stirring with two additional portions of MeOH (400 mL \times 2) and gently stirred in MeOH overnight. The polymer was then washed with stirring with additional portion of 400 mL of MeOH. The polymer was filtered and dried under vacuum to yield 13.99 g (wt% plasticizer_{grav.} = 79%) of a pale yellow, pliable polymer.

¹H NMR (500 MHz, CDCl₃, δ): 4.69–4.54 (br s), 4.54–4.38 (br m), 4.38–4.25 (br m), 4.25–4.12 (br s), 4.12–3.87 (br m), 3.74–3.65 (br m), 3.65–3.60 (br m), 3.60–3.55 (br m), 3.52 (q, J = 7.0 Hz),

2.54–2.22 (br m), 2.22–1.97 (br m), 1.97–1.79 (br m), 1.72–1.56 (br m), 1.52–1.43 (br m), 1.43–1.29 (br m), 1.21 (t, $J = 7.0$ Hz), 0.94 (t, $J = 7.4$ Hz). Based by ^1H NMR integration: (PBA + P2EEA) : PVC = 1.3 : 1.0; PBA : P2EEA = 3.0 : 1.0.

Preparation of PVC-g-50%PBA-co-50%P2EEA (14 g scale)

To a 50 mL Schlenk flask was added PVC (3.00 g, 48.0 mmol) and DMF (18 mL). The mixture was stirred and warmed slightly to fully dissolve the PVC. BA (8.60 mL, 60.0 mmol) and 2EEA (11.12 mL, 60.03 mmol) were added to the solution. To a 20 mL vial was added CuBr (206.18 mg, 1.4373 mmol). 6 mL of DMF was used to transfer CuBr to the PVC solution by pipet. PMDETA (0.30 mL, 1.43 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C while stirring under nitrogen. After 24 h, an aliquot was taken to analyze the crude reaction by ^1H NMR using CDCl_3 as solvent (%conv._{NMR} = 86%). The resulting polymer was diluted in 20 mL of THF and precipitated by addition to 400 mL of MeOH. The polymer was washed with stirring with two additional portions of MeOH (400 mL \times 2) and gently stirred in MeOH overnight. The polymer was then washed with stirring with additional portion of 400 mL). The polymer was filtered and dried under vacuum of MeOH to yield 13.14 g (wt% plasticizer_{grav.} = 77%) of a pale yellow, pliable polymer.

^1H NMR (500 MHz, CDCl_3 , δ): 4.68–4.54 (br s), 4.54–4.38 (br s), 4.38–4.25 (br m), 4.25–4.12 (br s), 4.12–3.90 (br s), 3.72–3.65 (br m), 3.65–3.60 (br m), 3.60–3.55 (br m), 3.52 (q, $J = 7.0$ Hz), 2.50–2.23 (br m), 2.23–1.98 (br m), 1.98–1.82 (br m), 1.72–1.57 (br m), 1.51–1.44 (br m), 1.44–

1.29 (br m), 1.21 (t, $J = 7.0$ Hz), 0.94 (t, $J = 7.3$ Hz). Based by ^1H NMR integration: (PBA + P2EEA) : PVC = 1.0 : 1.0; PBA : P2EEA = 1.0 : 1.0.

Preparation of PVC-g-25%PBA-co-75%P2EEA (14 g scale)

To a 50 mL Schlenk flask was added PVC (3.00 g, 48.0 mmol) and DMF (18 mL). The mixture was stirred and warmed slightly to fully dissolve the PVC. BA acrylate (4.30 mL, 30.0 mmol) and 2EEA (16.67 mL, 89.98 mmol) were added to the solution. To a 20 mL vial was added CuBr (206.22 mg, 1.4376 mmol). 6 mL of DMF was used to transfer CuBr to the PVC solution by pipet. PMDETA (0.30 mL, 1.43 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C while stirring under nitrogen. After 24 h, an aliquot was taken to analyze the crude reaction by ^1H NMR using CDCl_3 as solvent (%conv._{NMR} = 72%). The resulting polymer was diluted in 20 mL of THF and precipitated by addition to 400 mL of MeOH. The polymer was washed with stirring with two additional portions of MeOH (400 mL \times 2) and gently stirred in MeOH overnight. The polymer was then washed with stirring with additional portion of 400 mL of MeOH). The polymer was filtered and dried under vacuum to yield 13.66 g (wt% plasticizer_{grav.} = 78%) of a pale yellow, pliable polymer.

^1H NMR (500 MHz, CDCl_3 , δ): 4.59 (br s), 4.54–4.38 (br s), 4.38–4.26 (br m), 4.26–4.11 (br s), 4.04 (br s), 3.73–3.65 (br m), 3.63 (br s), 3.57 (br m), 3.52 (q, $J = 7.0$ Hz), 2.53–2.23 (br m), 2.23–1.98 (br m), 1.98–1.81 (br s), 1.75–1.59 (br m), 1.55–1.43 (br m), 1.37 (br m), 1.20 (t, $J = 7.0$ Hz), 0.94 (t, $J = 7.2$ Hz). Based by ^1H NMR integration: (PBA + P2EEA) : PVC = 1.0 : 2.9; PBA : P2EEA = 1.2 : 1.0.

Preparation of PVC-g-P2EEA (14 g scale)

To a 50 mL Schlenk flask was added PVC (3.00 g, 48.0 mmol) and DMF (18 mL). The mixture was stirred and warmed slightly to fully dissolve the PVC. 2EEA (22.23 mL, 120.0 mmol) was added to the solution. To a 20 mL vial was added CuBr (206.89 mg, 1.4422 mmol). 6 mL of DMF was used to transfer CuBr to the PVC solution by pipet. PMDETA (0.30 mL, 1.43 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C while stirring under nitrogen. After 24 h, an aliquot was taken to analyze the crude reaction by ^1H NMR using CDCl_3 as solvent ($\%_{\text{conv. NMR}} = 78\%$). The resulting polymer was diluted in 20 mL of THF and precipitated by addition to 400 mL of MeOH. The polymer was washed with stirring with two additional portions of MeOH (400 mL \times 2) and gently stirred in MeOH overnight. The polymer was then washed with stirring with another portion of 400 mL of MeOH. The polymer was filtered and dried under vacuum to yield 13.34 g ($\text{wt}\%_{\text{plasticizer}_{\text{grav.}}} = 78\%$) of a pale yellow, pliable polymer.

^1H NMR (500 MHz, CDCl_3 , δ): 4.64–4.54 (br s), 4.54–4.38 (br s), 4.38–4.26 (br m), 4.26–4.02 (br s), 3.73–3.65 (br m), 3.65–3.60 (br m), 3.60–3.55 (br m), 3.52 (q, $J = 7.0$ Hz), 2.51–2.23 (br s), 2.23–1.98 (br m), 1.98–1.84 (br s), 1.77–1.60 (br s), 1.50–1.38 (br m), 1.20 (t, $J = 7.0$ Hz). Based by ^1H NMR integration: P2EEA : PVC = 0.8 : 1.0.

RESULTS AND DISCUSSION

PVC graft copolymers were prepared by ATRP initiated from defect sites using 3 mol% CuBr, 3 mol% PMDETA as the ligand, and DMF as the solvent. The initial reaction mixture was deoxygenated using the freeze-pump-thaw method, followed by heating at 100 °C for 24 h. Five different ratios of BA and 2-(2-ethoxyethoxy)ethyl acrylate (2EEA) were investigated, ranging

from homopolymer grafts of each monomer, to 3 : 1 to 1 : 1 to 1 : 3 ratios, resulting in a series of PVC-*g*-(PBA-*co*-P2EEA) variants (**Table 1**). These ATRP graft polymerizations were initially conducted using 0.5 g of PVC, yielding approximately 2 g of PVC graft copolymer. To test the consistency and reproducibility of this ATRP method, all ratios were scaled up from 0.5 to 3.0 g of PVC, yielding approximately 14 g of final graft copolymer. Conversions were all higher than 70%, as calculated based on crude ¹H NMR spectra (the calculation method is shown in Supporting Information **Equation S1**). The work-up was done by precipitation in MeOH and serial washings of the resulting stirred solid polymer in additional MeOH. Defect sites on PVC were assumed to be the only initiating species for ATRP. Surprisingly, a control experiment without PVC did result in some polymer formation (**Table 1**, Entry 6, 23% conversion), which could be due to self-initiation of BA or 2EEA at 100 °C.^{54,55} This control reaction in the absence of PVC indicates that there may be some unattached polymer contaminating the PVC-*g*-PBA, PVC-*g*-(PBA-*co*-P2EEA), and PVC-*g*-P2EEA samples.

Table 1 Polymerization conditions and percent conversion^a

Entry	[PVC]/[BA]/[2EEA]/[CuBr]/[PMDETA] ^b	Initial ration of [BA]/[2EEA]	Conv% _{NMR} ^c (2 g scale)	Conv% _{NMR} ^c (14 g scale)
1	1 : 2.5 : 0 : 0.03 : 0.03	BA only	81%	88%
2	1 : 1.9 : 0.6 : 0.03 : 0.03	3 : 1	73%	88%
3	1 : 1.3 : 1.3 : 0.03 : 0.03	1 : 1	84%	86%
4	1 : 0.6 : 1.9 : 0.03 : 0.03	1 : 3	80%	72%
5	1 : 0 : 2.5 : 0.03 : 0.03	2EEA only	80%	80%
6	0 : 1.3 : 1.3 : 0.03 : 0.03 ^d	1 : 1	23% ^e	-

^aAll polymerizations were conducted at 100 °C in DMF for 24 h; ^bRatios were calculated in mol; ^cConversion of total monomer; polymers were not completely soluble in the CDCl₃ NMR solvent; ^dControl without PVC; ^eSample was completely soluble in the CDCl₃ NMR solvent.

Characterization by FTIR, and ^1H NMR spectroscopies, and GPC of the functionalized PVC graft copolymers provided important structural information. All five modified polymers show a distinctive ester carbonyl peak around 1740 cm^{-1} in the FTIR (**Figure 2**), confirming the incorporation of acrylates into these modified PVC samples.

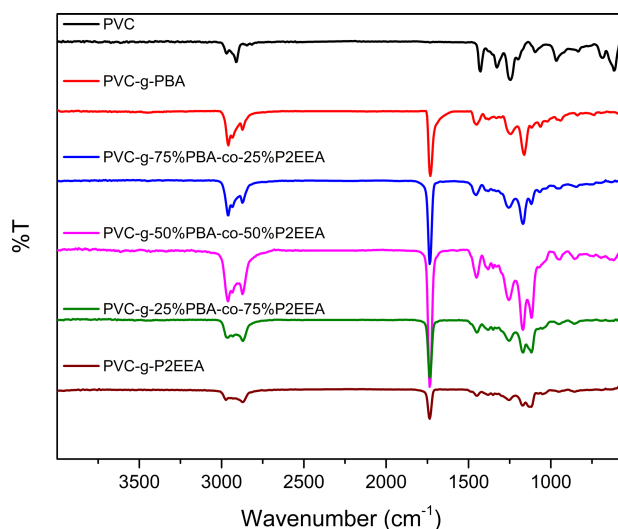


Figure 2 FTIR of PVC-*g*-PBA, PVC-*g*-(PBA-co-P2EEA), and PVC-*g*-P2EEA graft polymers

In the ^1H NMR spectra (**Figure 3**), the CH-Cl methine protons of PVC appear at 4.6-4.2 ppm (**Figure 3**, proton a), the $-\text{CH}_2-\text{O}-\text{C}=\text{O}$ methylene protons of PBA are seen at 4.0 ppm (**Figure 3**, proton c), and the $-\text{CH}_2-\text{O}-\text{C}=\text{O}$ methylene protons of P2EEA have a chemical shift of 4.2 ppm (**Figure 3**, proton c'). The NMR data clearly demonstrate the presence of PVC and PBA and/or P2EEA in the graft copolymers.

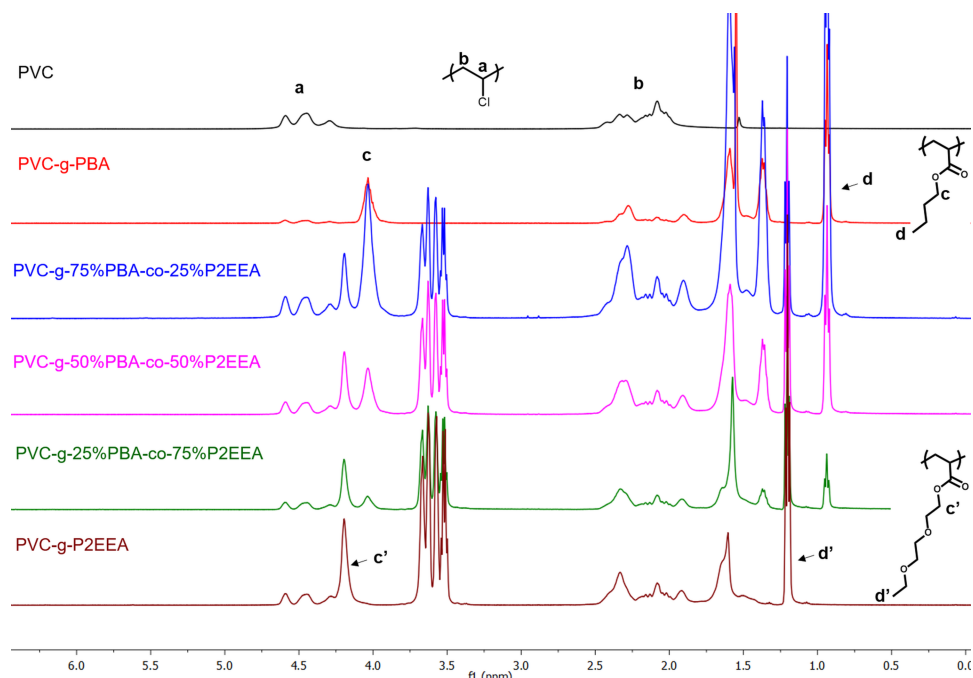


Figure 3 ^1H NMR spectra of PVC-*g*-PBA, PVC-*g*-(PBA-*co*-P2EEA), PVC-*g*-P2EEA polymers

Information on the composition and relative size of the new grafts as determined by ^1H NMR is summarized in **Table 2**. The ratio of integration of the CH-Cl methine protons (**Figure 3**, proton **a**) of PVC, of the $-\text{CH}_2\text{-O-C=O}$ methylene protons (**Figure 3**, proton **c**) of PBA, and of the $-\text{CH}_2\text{-O-C=O}$ methylene protons (**Figure 3**, proton **c'**) of P2EEA were used to determine the degree of functionalization. The ratio of PBA and P2EEA were calculated based on the integration of the methyl protons of PBA at 0.9 ppm (**Figure 3**, proton **d**) and the methyl protons of P2EEA at 1.2 ppm (**Figure 3**, proton **d'**). The amount of incorporated acrylates monomers was very close to the initial monomer concentrations, indicating the two monomers have similar reactivity ratios in ATRP. Interestingly, the relative length of the polyacrylate graft (a combination of PBA and polyether) decreases with increasing amounts of 2EEA monomer, from PBA : PVC = 1.6 : 1.0 (for 100% BA) to P2EEA : PVC = 1.0 : 1.0 (for 100% 2EEA). This may be an

artifact of the work-up procedure, in which the precipitated polymer was sequentially washed several times with MeOH, preferentially dissolving the P2EEA rich copolymers. The PVC graft copolymer samples were not completely soluble in the CDCl₃ NMR solvent, indicating some polymer fractionation, and suggesting that the ratios obtained by NMR are not completely accurate.

Table 2 Composition of graft copolymers based on ¹H NMR analysis

Monomer Ratio used BA : 2EEA	Polymer P(BA) : P(2EEA) ^a (2 g and 14 g scale)	Graft (PBA+P2EEA) : PVC ^a (2 g scale)	Graft (PBA+P2EEA) : PVC ^a (14 g scale)
BA only	BA only	1.6 : 1.0	1.4 : 1.0
75% : 25%	3.0 : 1.0	1.4 : 1.0	1.3 : 1.0
50% : 50%	1.0 : 1.0	1.3 : 1.0	1.0 : 1.0
25% : 75%	1.0 : 2.9	1.1 : 1.0	1.2 : 1.0
2EEA only	2EEA only	1.0 : 1.0	0.8 : 1.0

^aBy ¹H NMR integration; samples were not completely soluble in the CDCl₃ NMR solvent. The NMR results represent only the soluble portion of the sample structure.

The weight percent of total plasticizer based on gravimetry (the calculation method is shown in Supporting Information **Equation S2**) is 73 – 80% for all samples (**Table 3**). Similar results on both 2 g and 14 g scales demonstrate the reproducibility and easy scale-up of this simple ATRP modification of PVC, indicating that this one step self-plasticization method can be industrially relevant.

Table 3 Weight percent plasticizer

Samples	Wt% plasticizer (grav.) (2 g scale)	Wt% plasticizer (grav.) (14 g scale)
PVC- <i>g</i> -PBA	80%	80%
PVC- <i>g</i> -75%PBA- <i>co</i> -25%P2EEA	75%	79%
PVC- <i>g</i> -50%PBA- <i>co</i> -50%P2EEA	75%	77%
PVC- <i>g</i> -25%PBA- <i>co</i> -75%P2EEA	73%	78%
PVC- <i>g</i> -P2EEA	73%	78%

The thermal properties of the internally plasticized PVC were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). For both 2 g and 14 g scale samples, the DSC and TGA data are very similar. Herein will be presented the data for the larger-scale materials (data for 2 g samples are provided in the Supporting Information). DSC show a single T_g value for all samples, indicating the absence of phase separation (**Figure 4** and **Table 4**). All of these functionalized PVC polymers exhibit good flexibility when handled, and all T_g values are below 0 °C. The PVC-*g*-PBA sample displayed a slightly less impressive T_g value of -25 °C. The T_g decreases with increasing amounts of P2EEA. The lowest T_g value achieved was -50 °C for PVC-*g*-25%PBA-*co*-75%P2EEA. The slightly higher T_g values of PVC-*g*-P2EEA than PVC-*g*-25%PBA-*co*-75%P2EEA with the same wt% percent plasticizer (78%, **Table 3**) might be an artifact of the workup procedure, which preferentially dissolves and washes away P2EEA-rich copolymers. Comparison of PVC-*g*-75%PBA-*co*-25%P2EEA with PVC-*g*-PBA shows that addition of 25% P2EEA leads to a significant decrease of T_g from -25 °C to -38 °C. Further increasing the amount of P2EEA leads to diminishing decreases in T_g values. PVC-*g*-25%PBA-*co*-75%P2EEA and PVC-*g*-P2EEA have very similar T_g values. Considering that monomer 2EEA is more expensive (2EEA: \$0.20/g; BA: \$0.04/g), BA : 2EEA = 3 : 1 yielding PVC-*g*-75%PBA-*co*-25%P2EEA is an attractive ratio when taking both price and plasticizing efficiency into account. Plasticization efficiencies^{26,56} are summarized in the Supp. Info (**Table S1**), all showing values higher than 70%. Plasticization efficiency increases with increasing percentage of P2EEA ratio, attesting to the efficiency of the polyether functionality as PVC plasticizer.^{13,14,26,27}

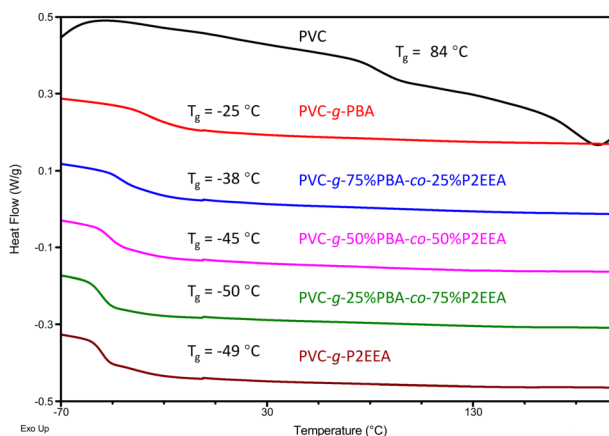


Figure 4 DSC (2nd heat cycle) of PVC graft copolymers on the 14 g scale (see Supporting Information Figure S1 for very similar results for sample prepared on the 2 g scale)

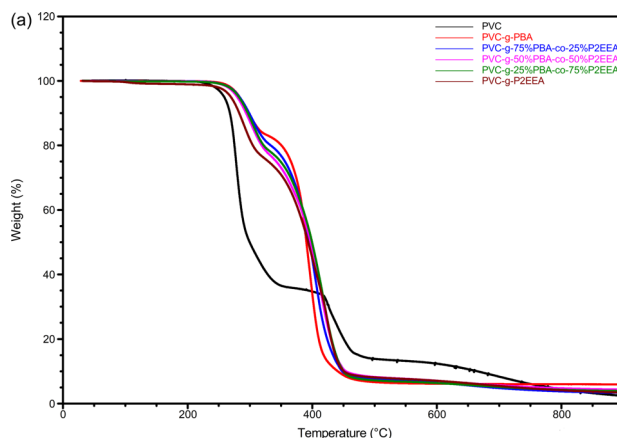
Table 4 DSC and TGA data of PVC graft copolymers^a

Grafts on PVC	T_g (°C)	Onset temp. (°C)	Temp. at 5% weight loss (°C)	Mass loss First stage(%)	Mass loss second stage(%)	Mass loss third stage(%)	Residue (%) at 900 °C	$T_{d,1}$ (°C)	$T_{d,2}$ (°C)
None	84.3	261.4	258.7	64.2	22.3	11.0	2.5	278.2	426.57
PBA	25.3	271.0	283.4	16.9	71.8	5.3	6.0	297.3	397.1
75%PBA	38.4	269.4	283.3	20.0	72.8	3.8	3.4	303.4	404.1
50%PBA	44.7	269.6	279.6	23.0	69.3	3.4	4.4	303.0	414.1
25%PBA	49.6	272.7	282.3	21.9	71.4	2.9	3.9	304.9	418.9
P2EEA	48.9	265.03	269.4	23.2	37.2	30.8 ^b	3.5	290.1	398.8 ^c

^aSamples made on the 14 g scale (see Supporting Information Table S1 for very similar results from samples prepared on the 2 g scale); ^bMass loss fourth stage = 4.4%; ^c $T_{d,3}$ = 424.4 °C.

TGA was used to examine the thermal stabilities of the modified polymers (**Figure 5** and **Table 4**). PVC has a two-stage degradation below 500 °C.⁵⁷ The first stage occurs at ~260 °C due to dehydrochlorination. The second stage starts at ~410 °C, taking apart the rest of the polymer backbone. Polyvinyl acrylates such as PBA degrade in a one-stage process starting at ~300 °C.⁵⁸

The grafted PVC copolymers predominantly display a two-stage decomposition process, except for PVC-*g*-P2EEA, which showed three stages. The first stage is from ~270 °C to ~320 °C, with a weight loss ranging from 17% to 23%. This is likely caused by dehydrochlorination. At ~320 °C, the degradation is dominated by the polyacrylate portion. In **Table 4**, the PVC graft copolymers have higher onset decomposition temperatures and higher temperatures at 5% weight loss compared to unmodified PVC. This is expected, as the reactive tertiary and allylic chlorine atoms at defect sites are most susceptible to dehydrochlorination, contributing to the initial thermal instability of PVC below ~300 °C.⁵⁹ Replacement of these reactive tertiary and allylic chlorine atoms with carbon grafts by ATRP results in enhanced thermal stability. Adding a significant portion of polyacrylate (PBA and/or P2EEA) to PVC is expected to lead to a higher temperature at 5% weight loss due to the higher thermal stability of polyacrylates versus PVC.



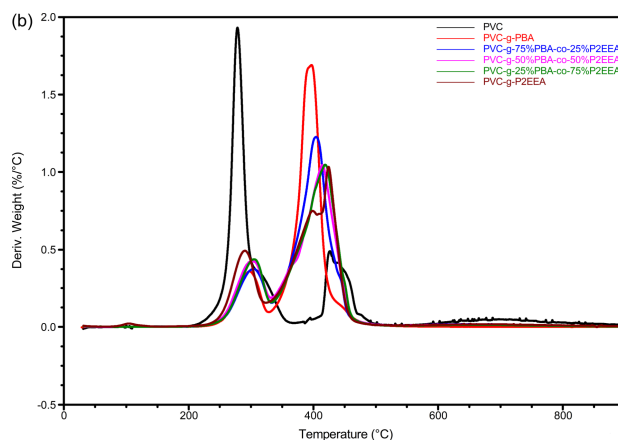


Figure 5 a) TGA curves and b) DTG curves (14 g scale)

The PVC graft copolymers were analyzed by GPC (**Figure 6**). The GPC traces for the 2 g scale samples are shown in the Supp. Info (**Figure S4**). Compared to unmodified PVC, the retention times of all of the PVC graft copolymers are slightly decreased, reflecting their higher weights and volumes. The peak sizes of the PVC graft copolymers are significantly less than those of unmodified PVC. This may be due to the poor solubilities of the PVC graft copolymers in THF, indicative of possible crosslinking during the 24 h polymerization. These graft copolymers were also poorly soluble in common solvents including DMF and NMP. Interestingly, PVC-*g*-PBA shows a bimodal distribution. Some of these polymers show a shoulder corresponding to unmodified PVC, indicating that some unreacted PVC homopolymer may remain in the reaction. M_p , M_w , and M_z values of the functionalized PVC samples are significantly larger compared to PVC (**Table 5**). The M_n values for several the 14 g scale graft copolymers are smaller than the apparent M_n values for unmodified PVC. This is likely due to poor solubility of the large molecular weight, possibly crosslinked polymers, leaving a majority of the smaller polymers in solution. In addition, it is important to note the inaccuracy of using

linear polystyrene as molecular weight standards for these polymer brushes. The graft copolymers are a dense, structurally complex species that take up volume in a manner far different from a linear polymer chain. The polydispersity of PVC graft copolymer samples vary widely. However, a low PDI is not required for high plasticization efficiency. Having variable sized grafts should increase the disorder of the material, and thus enhance the plasticity.

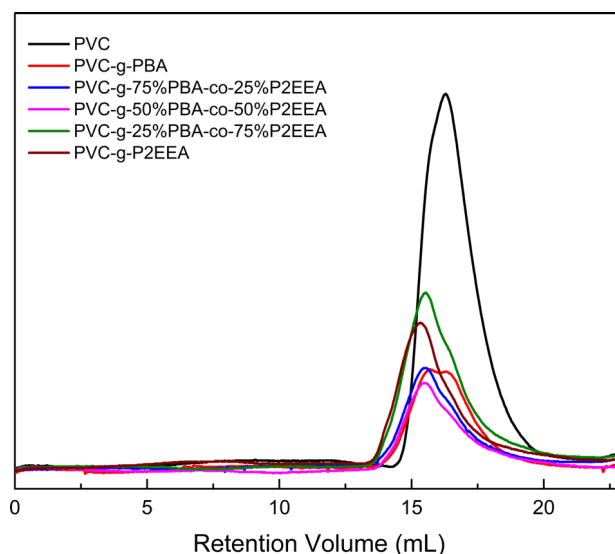


Figure 6 GPC traces of PVC graft copolymers (14 g scale)

Table 5 GPC of PVC and the resulting graft copolymers^a

Samples	M_p	M_n	M_w	M_z	PD
PVC	68,900	36,400	73,100	114,400	2.0
PVC- <i>g</i> -PBA	112,500	34,000	108,200	244,300	3.2
PVC- <i>g</i> -75%PBA- <i>co</i> -25%P2EEA	137,300	44,600	140,500	286,500	3.2
PVC- <i>g</i> -50%PBA- <i>co</i> -50%P2EEA	140,700	30,800	133,000	277,600	4.3
PVC- <i>g</i> -25%PBA- <i>co</i> -75%P2EEA	135,600	30,000	136,900	289,800	4.6
PVC- <i>g</i> -P2EEA	163,600	34,300	165,600	342,200	4.8

^aResults are from samples prepared on the 14 g scale (see Supporting Information **Table S3** for results from samples prepared on the 2 g scale)

One concern with using Cu-catalyzed ATRP is the residual copper catalyst in the resulting polymer. For example, on the 14 g scale, approximately 200 mg of CuBr was used. Although the graft co-polymer samples were washed with methanol several times to remove both catalyst

and ligand, some polymers still had a faint green color, indicating residual copper. This contamination limits the applications of these polymers in medical devices and food packaging. Efforts aimed at reducing the amount of copper, for example following Matyjaszewski's work with activated ligands³⁵, are ongoing in our lab.

CONCLUSIONS

A series of PVC-*g*-(PBA-*co*-P2EEA) polymers were prepared by ATRP in a single step, resulting in materials with T_g values as low as -50 °C. Several conclusions can be drawn from this systematic study. Most importantly, all of these internally plasticized PVC graft copolymers were homogeneous (non-phase separated) materials, as reflected by a single T_g temperature. Pendant polyether grafts are more efficient plasticizers compared to pendant poly(*n*-butyl ester) grafts. This is the first time that polyether grafts have been attached to PVC via ATRP to achieve very low T_g values without phase separation. In addition to highly effective internal plasticization, these graft copolymers display enhanced thermal stability, as the ATRP process removes the particularly labile tertiary and allylic chlorine atoms at the defect sites. The graft polymerization was carried out initially on 0.5 g of PVC, forming about 2 g of derivatized PVC. This was easily scaled up to form 14 g of plasticized PVC; more importantly, similar properties of polymers were observed at both scales. This bodes well for the scalability of this process, which should be applicable on an industrial level. Overall, the internal plasticization of PVC has been successfully demonstrated using operationally simple ATRP to give flexible, homogeneous graft copolymers.

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REFERENCES AND NOTES

1. Carroll, W. F.; Johnson, R. W.; Moore, S. S.; Paradis, R. A. In *Applied Plastics Engineering Handbook (Second Edition)*; Kutz, M., Ed.; William Andrew Publishing: Cambridge, **2017**; Chapter 4, pp 73–89.
2. Chiellini, F.; Ferri, M.; Morelli, A.; Dipaola, L.; Latini, G. *Prog. Polym. Sci.* **2013**, *38* (7), 1067–1088.
3. Rowdhwal, S. S. S.; Chen, J. *BioMed Res. Int.* **2018**, *2018*, 1750368.
4. Schettler, T. *Int. J. Androl.* **2006**, *29*, 134–139.
5. Heudorf, U.; Mersch-Sundermann, V.; Angerer, J. *Child. Environ. Cent. Eur. - Threats Chances* **2007**, *210*, 623–634.
6. Desdoits-Lethimonier, C.; Lesné, L.; Dejuçq-Rainsford, N.; Albert, O.; Jégou, B.; Guillé, F.; Le Bizec, B.; Courant, F.; Zalko, D.; Perdu, E. *Hum. Reprod.* **2012**, *27*, 1451–1459.
7. Xie, C.; Zhao, Y.; Gao, L.; Chen, J.; Cai, D.; Zhang, Y. *Mol. Cell. Endocrinol.* **2015**, *407*, 67–73.
8. Axelsson, J.; Rylander, L.; Rignell-Hydbom, A.; Lindh, C. H.; Jönsson, B. A. G.; Giwercman, A. *Environ. Res.* **2015**, *138*, 264–270.
9. Giulivo, M.; Lopez de Alda, M.; Capri, E.; Barceló, D. A Review. *Environ. Res.* **2016**, *151*, 251–264.
10. Mijangos, C.; Martinez, A.; Michel, A. *Eur. Polym. J.* **1986**, *22*, 417–421.
11. Navarro, R.; Pérez Perrino, M.; Gómez Tardajos, M.; Reinecke, H. *Macromolecules* **2010**, *43*, 2377–2381.
12. Navarro, R.; Perrino, P. M.; García, C.; Elvira, C.; Gallardo, A.; Reinecke, H. *Polymers* **2016**, *8*, 152.
13. Navarro, R.; Gacal, T.; Ocakoglu, M.; García, C.; Elvira, C.; Gallardo, A.; Reinecke, H. *Macromol. Rapid Commun.* **2017**, *38*, 1600734.
14. Navarro, R.; Pérez Perrino, M.; García, C.; Elvira, C.; Gallardo, A.; Reinecke, H. *Macromolecules* **2016**, *49*, 2224–2227.
15. Jia, P.; Hu, L.; Yang, X.; Zhang, M.; Shang, Q.; Zhou, Y. *RSC Adv.* **2017**, *7*, 30101–30108.
16. Jia, P.; Hu, L.; Shang, Q.; Wang, R.; Zhang, M.; Zhou, Y. *ACS Sustain. Chem. Eng.* **2017**, *5*, 6665–6673.
17. Jia, P.; Zhang, M.; Hu, L.; Song, F.; Feng, G.; Zhou, Y. *Sci. Rep.* **2018**, *8*, 1589.
18. Yang, P.; Yan, J.; Sun, H.; Fan, H.; Chen, Y.; Wang, F.; Shi, B. *RSC Adv.* **2015**, *5*, 16980–16985.
19. Demirci, G.; Tasdelen, M. A. *Eur. Polym. J.* **2015**, *66*, 282–289.
20. Lee, K. W.; Chung, J. W.; Kwak, S.-Y. *Macromol. Rapid Commun.* **2016**, *37*, 2045–2051.
21. Jia, P.; Hu, L.; Feng, G.; Bo, C.; Zhang, M.; Zhou, Y. *Mater. Chem. Phys.* **2017**, *190*, 25–30.
22. Jia, P.; Wang, R.; Hu, L.; Zhang, M.; Zhou, Y. *Pol. J. Chem. Technol.* **2017**, *19*, 16–19.
23. Earla, A.; Li, L.; Costanzo, P.; Braslau, R. *Polymer* **2017**, *109*, 1–12.
24. Chu, H.; Ma, J. *Korean J. Chem. Eng.* **2018**, *35*, 2296–2302.
25. Jia, P.; Ma, Y.; Feng, G.; Hu, L.; Zhou, Y. *J. Clean. Prod.* **2019**, *227*, 662–674.
26. Higa, C. M.; Tek, A. T.; Wojtecki, R. J.; Braslau, R. *J. Polym. Sci. Part Polym. Chem.* **2018**, *56*, 2397–2411.
27. Li, L.; Tek, A. T.; Wojtecki, R. J.; Braslau, R. *J. Polym. Sci. Part Polym. Chem.* **2019**, *57*, 1821–1835.
28. Coelho, J. F. J.; Carreira, M.; Popov, A. V.; Gonçalves, P. M. O. F.; Gil, M. H. *Eur. Polym. J.* **2006**, *42*, 2313–2319.
29. Coelho, J. F. J.; Carreira, M.; Gonçalves, P. M. O. F.; Popov, A. V.; Gil, M. H. *J. Vinyl Addit. Technol.* **2006**, *12*, 156–165.

30. Rezende, T. C.; Abreu, C. M. R.; Fonseca, A. C.; Higa, C. M.; Li, L.; Serra, A. C.; Braslau, R.; Coelho, J. F. J. *Polymer* **2020**, *196*, 122473.
31. Sun, Z.; Choi, B.; Feng, A.; Moad, G.; Thang, S. H. *Macromolecules* **2019**, *52*, 1746–1756.
32. Chang, Y.; Pan, M.; Yuan, J.; Liu, Y.; Wang, X.; Jiang, P.; Wang, Y.; Zhong, G.-J.; Li, Z.-M. *RSC Adv.* **2015**, *5*, 40076–40087.
33. Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
34. Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015–4039.
35. Matyjaszewski, K.; Tsarevsky, N. V. *J. Am. Chem. Soc.* **2014**, *136*, 6513–6533.
36. Jenkins, A. D.; Jones, R. G.; Moad, G. *Pure Appl. Chem.* **2009**, *82*, 483–491.
37. Paik, H.; Gaynor, S. G.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1998**, *19*, 47–52.
38. Percec, V.; Asgarzadeh, F. J. *Polym. Sci. Part Polym. Chem.* **2001**, *39*, 1120–1135.
39. Percec, V.; Cappotto, A.; Barboiu, B. *Macromol. Chem. Phys.* **2002**, *203*, 1674–1683.
40. Bicak, N.; Ozlem, M. *J. Polym. Sci. Part Polym. Chem.* **2003**, *41*, 3457–3462.
41. Bicak, N.; Karagoz, B.; Emre, D. *J. Polym. Sci. Part Polym. Chem.* **2006**, *44*, 1900–1907.
42. Coşkun, M.; Barim, G.; Demirelli, K. *J. Macromol. Sci. Part A* **2007**, *44*, 475–481.
43. Ahn, S. H.; Seo, J. A.; Kim, J. H.; Ko, Y.; Hong, S. U. *J. Membr. Sci.* **2009**, *345*, 128–133.
44. Patel, R.; Patel, M.; Ahn, S. H.; Sung, Y. K.; Lee, H.-K.; Kim, J. H.; Sung, J.-S. *Mater. Sci. Eng. C* **2013**, *33*, 1662–1670.
45. Fang, L.-F.; Matsuyama, H.; Zhu, B.-K.; Zhao, S. *J. Appl. Polym. Sci.* **2018**, *135*, 45832. <https://doi.org/10>
46. Lanzalaco, S.; Galia, A.; Lazzano, F.; Mauro, R. R.; Scialdone, O. *J. Polym. Sci. Part Polym. Chem.* **2015**, *53*, 2524–2536.
47. Huang, Z.; Feng, C.; Guo, H.; Huang, X. *Polym. Chem.* **2016**, *7*, 3034–3045.
48. Liu, K.; Pan, P.; Bao, Y. *RSC Adv.* **2015**, *5*, 94582–94590.
49. Wypych, G. In *PVC Degradation and Stabilization (Third Edition)*; Wypych, G., Ed.; ChemTec Publishing: Boston, **2015**; Chapter 1, pp 1–23.
50. Dean, L.; Dafei, Z.; Deren, Z. *Polym. Degrad. Stab.* **1988**, *22*, 31–41.
51. Xie, T. Y.; Hamielec, A. E.; Rogestedt, M.; Hjertberg, T. *Polymer* **1994**, *35*, 1526–1534.
52. Rogestedt, M.; Hjertberg, T. *Macromolecules* **1993**, *26*, 60–64.
53. Azzam, T.; Eisenberg, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 7443–7447.
54. Srinivasan, S.; Kalfas, G.; Petkovska, V. I.; Bruni, C.; Grady, M. C.; Soroush, M. *J. Appl. Polym. Sci.* **2010**, *118*, 1898–1909.
55. Moghadam, N.; Liu, S.; Srinivasan, S.; Grady, M. C.; Soroush, M.; Rappe, A. M. *J. Phys. Chem. A* **2013**, *117*, 2605–2618.
56. Lee, K. W.; Chung, J. W.; Kwak, S.-Y. *Green Chem.* **2016**, *18*, 999–1009.
57. McNeill, I. C.; Memetea, L.; Cole, W. J. *Polym. Degrad. Stab.* **1995**, *49*, 181–191.
58. Grassie, N.; Speakman, J. G. *J. Polym. Sci. [A1]* **1971**, *9*, 919–929.
59. Wypych, G. In *PVC Degradation and Stabilization (Third Edition)*; Wypych, G., Ed.; ChemTec Publishing: Boston, **2015**; Chapter 4, pp 79–165

GRAPHICAL ABSTRACT

