Advances in Internal Plasticization of PVC: Copper-Mediated Atom-Transfer Radical Polymerization from PVC Defect Sites To Form Acrylate Graft Copolymers

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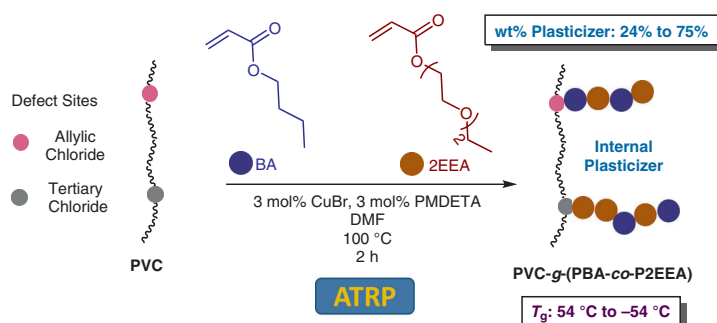rbraslau@ucsc.edu
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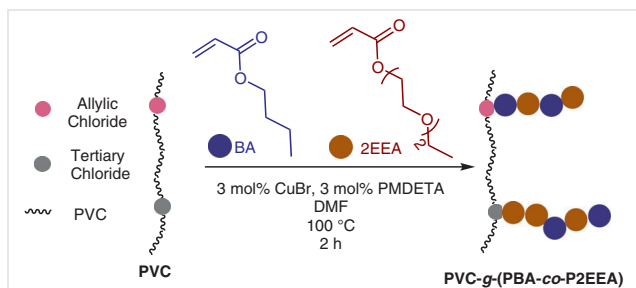
Abstract Internally plasticized PVC copolymers were prepared by grafting PVC with butyl acrylate and 2-(2-ethoxyethoxy)ethyl acrylate by atom-transfer radical polymerization, resulting in well-behaved polymers with a wide range of glass transition temperatures (–54 °C to 54 °C). When the grafted side chains made up more than 50% of the polymer by weight, the glass transition temperatures were below 0 °C. The covalent attachment of the plasticizing grafts requires one simple procedure starting from commercial PVC, making this strategy an industrially relevant and environmentally friendly alternative to the use of conventional small-molecule plasticizers.

Key words polyvinyl chloride, copper catalysis, atom-transfer radical polymerization, graft copolymerization, butyl acrylate, ethoxyethoxyethyl acrylate

Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastics. Because pure PVC is rigid and brittle, plasticizers are used to increase the flexibility of PVC materials for a variety of applications, such as toys, medical devices, sports equipment, or building materials.[1] Commonly used small-molecule plasticizers such as phthalates can migrate out of the PVC matrix;[2] resulting not only in degradation of mechanical properties, but also in health issues arising from exposure to these molecules. The covalent attachment of plasticizers to PVC prevents plasticizer migration. Strategies to attach plasticizing moieties include nucleophilic substitution of the secondary chlorides on the PVC chains, as well as various polymerizations. Studies using the nucleophilic-substitution approach have focused on sulfides,[3,4] amines,[5] and azides (to form triazole linkages).[6–16]

Previous work in this laboratory highlighted the use of thermal azide/alkyne Huisgen cycloadditions to attach plasticizers to PVC.[6,12,14,15] However, the nucleophilic-substitution approach to attaching plasticizers requires at least three synthetic steps from PVC, which is impractical on an industrial scale.

Polymerization offers alternative approaches to covalent attachment of plasticizers to PVC. Copolymerization of vinyl chloride (VC) with monomers bearing plasticizers has been accomplished to give either block or random copolymers. Examples include block copolymers of PVC with poly(butyl acrylate) (PBA)[17,18] or poly(ε-caprolactone).[19] In collaboration with Coelho,[20] we have used random copolymerization of VC with an acrylate bearing a mimic of di-2-ethylhexyl phthalate (DEHP), the most common PVC plasticizer. Alternatively, an attractive strategy involves the use of atom-transfer radical polymerization (ATRP)[21] to grow graft copolymers from PVC chains.[22–33] Commercial PVC contains allylic and tertiary chloride defect moieties in the backbone.[34] Percec and Asgarzadeh[23] demonstrated the first application of copper-mediated ATRP initiated from these active sites, resulting in glass-transition temperature (T_g) values as low as –4 °C. We recently demonstrated the use of acrylates in ATRP from PVC to prepare PVC graft copolymers by employing PBA and poly[2-(2-ethoxyethoxy)ethyl acrylate] (P2EEA) to form flexible homogeneous PVC graft copolymers.[35] Our initial ATRP reactions were carried out for over 24 hours, affording graft copolymers that were only partially soluble in THF, DMF, or NMP, probably due to cross-linking. Here we report the preparation of soluble internally plasticized PVC graft copolymers under improved conditions (Scheme 1). A variety of graft lengths were ex-

Scheme 1 Formation of internally plasticized graft copolymers by ATRP from defect sites on PVC

plored to generate graft copolymers with tunable flexibilities for a variety of applications.

In our previous study,[35] a control experiment was performed in the absence of PVC, indicating that up to 23% homopolymerization occurred. To minimize both this competing nongraft polymerization as well as undesired cross-linking, the reaction duration was decreased from 24 hours to 2 hours. Control reactions were conducted without PVC for each monomer (BA and 2EEA) using 3 mol% of CuBr, and 3 mol% of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) in DMF at 100 °C. Nongrafted homopolymer was formed in only 10% yield for BA and 6% for 2EEA (Table 1, entries 1 and 2), significantly less than the 23% obtained after 24 hours. A series of graft copolymers were then prepared by using a polymerization time of two hours (entries 3–7).[36] Five different monomer ratios (BA/2EEA) were investigated, resulting in good conversions, ranging from 56 to 78%. More importantly, all these materials were soluble in CDCl$_3$, suggesting an absence of cross-linking.

Table 1 Graft Polymerizations: Percentage Conversions[a]

Entry	[PVC]/[BA]/[2EEA]/[CuBr]/[PMDETA][b]	Conv.[c] (%)
1	0:**2.5**:**0**:0.03:0.03	10
2	0:**0**:**2.5**:0.03:0.03	6
3	1:**2.5**:**0**:0.03:0.03	78
4	1:**1.9**:**0.6**:0.03:0.03	61
5	1:**1.3**:**1.3**:0.03:0.03	60
6	1:**0.6**:**1.9**:0.03:0.03	56
7	1:**0**:**2.5**:0.03:0.03	60

[a] All polymerizations were conducted at 100 °C in DMF for 2 h.
[b] Initial molar ratios.
[c] Conversion of total monomers, as determined by ^{1}H NMR.

^{1}H NMR was used to characterize the monomer ratios in the PVC grafts (Table 2). The monomer-ratio calculation method is shown in the Supporting Information (SI). Two main trends were found: (1) the PBA/P2EEA ratios in the grafts were close to the initial BA/2EEA monomer ratios, and (2) PVC-*g*-PBA had the highest polyacrylate graft length

(PBA/PVC = 1.4:1.0). The other graft copolymers all showed similar polyacrylate lengths of approximately graft/PVC = 1:1. This is consistent with the percentage conversions as determined by ^{1}H NMR (Table 1) and from the gravimetric yields (SI; Table S1). Not surprisingly, the percentage conversions by ^{1}H NMR before workup were higher than the gravimetric yields after workup due to loss of nongrafted polymer and general material loss. The workup entailed precipitation of the crude polymer in MeOH; MeOH-soluble fractions were therefore lost. PVC-*g*-PBA shows pre-workup values that were closer to the to post-workup yields, as nongrafted PBA is only partially soluble in MeOH, whereas the more polyether rich homopolymers and graft copolymers were more likely to be washed away during precipitation from MeOH.

Table 2 Composition of Graft Copolymers Based on ^{1}H NMR Integration

Entry	Initial molar ratio [BA]/[2EEA]	Polymer molar ratio PBA/P2EEA	Polymer molar ratio (PBA + P2EEA)/PVC
1	BA only	PBA only	1.4:1.0
2	3:1	3.0:1.0	1.0:1.0
3	1:1	1.0:1.0	0.9:1.0
4	1:3	1.0:2.8	0.9:1.0
5	2EEA only	P2EEA only	0.9:1.0

The T_g values of these internally plasticized PVC graft copolymers were measured by differential scanning calorimetry (DSC), using data from the second heating cycle. PVC graft copolymers made with molar ratios of 2.5:1.0 had very low T_g values compared with PVC (T_g = 84 °C) (Figure 1). Only a single T_g was observed, indicating that there was no microphase separation. The least depressed T_g was seen for PVC-*g*-PBA (T_g = –25 °C), and the lowest T_g value was observed for PVC-*g*-25%PBA-*co*-75%P2EEA (T_g = –54 °C). This is consistent with our previous observation that 2EEA-rich grafts are more efficient plasticizers compared with those rich in BA. Some of the materials showed a melting temperature (T_m) indicating these copolymers exhibit semi-crystallinity, along with very low T_g values (SI; Table S4).

Thermogravimetric analysis (TGA) (Figure 2) and derivative thermogravimetry (DTG) (SI; Figure S4 and Table S2) of these internally plasticized PVC materials were used to examine their thermal stabilities. PVC and PVC bearing polyacrylate grafts exhibited two main stages of degradation. The onset temperatures of the modified PVC samples were higher than those of unmodified PVC, because the unstable allylic and tertiary chloride defect sites were replaced by carbon grafts.[37] The thermal stabilities of the PBA and P2EEA grafts were similar.

Gel-permeation chromatography (GPC) traces of these PVC graft copolymers are shown in Figure 3. Compared with unmodified PVC, the retention times were shorter and
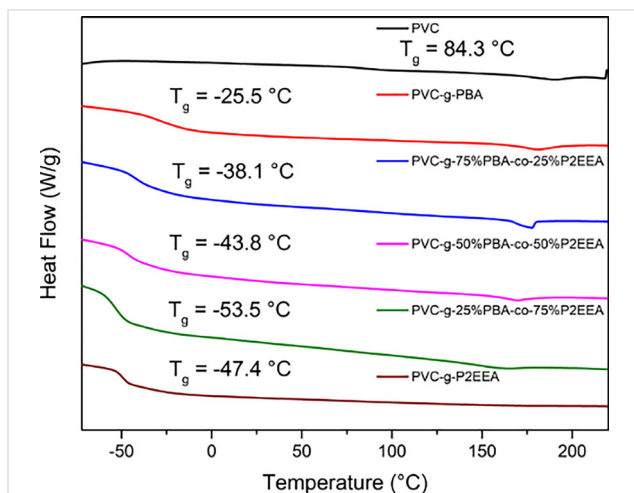
Figure 1 DSC (second heating cycle) of PVC graft copolymers made with a monomer-to-vinyl chloride unit ratio = 2.5:1.0. The slightly lower T_g value of PVC-*g*-25%PBA-*co*-75%P2EEA (wt% plasticizer$_{grav}$ = 68%) compared with PVC with full polyether grafts PVC-*g*-P2EEA (wt% plasticizer$_{grav}$ = 70%) is probably an artifact resulting from the workup procedure, which preferentially dissolves 2EEA-rich copolymers.
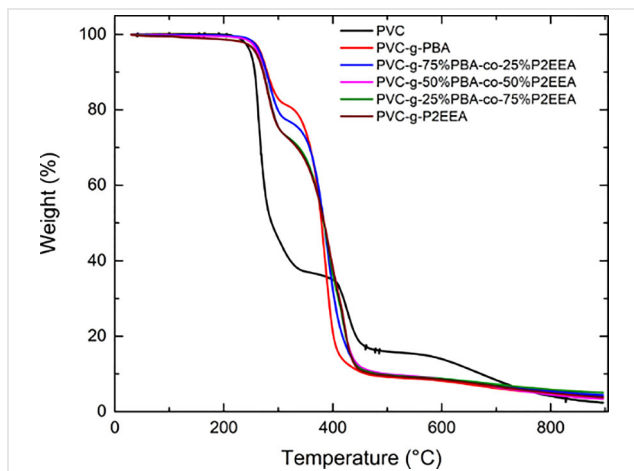

Figure 2 TGA curves of internally plasticized PVC samples made with a monomer-to-VC unit ratio of 2.5:1.0

Figure 3 GPC traces of PVC graft copolymers made with a monomer-to-VC unit ratio of 2.5:1.0

Table 3 Graft Polymerizations using Lower Ratios of Acrylates to VC Units: Percent Conversion[a]

Entry	[PVC]/[BA]/[2EEA]/[CuBr]/[PMDETA][b]	Conv.[c] (%)
1	1:**0.5:0**:0.03:0.03	59
2	1:**1.0:0**:0.03:0.03	67
3	1:**0:0.5**:0.03:0.03	40
4	1:**0:1.0**:0.03:0.03	59

[a] All polymerizations were conducted at 100 °C in DMF for 2 h.
[b] Initial ratios calculated in moles.
[c] Conversion of total monomers determined by ^{1}H NMR.

the values of various weighted averages of molecular weight M_p, M_n, M_w, and M_z of the functionalized PVC samples were significantly higher than those of unmodified PVC (SI; Table S3), reflecting their higher weights and effective volumes. Most of the new polymers had a unimodal distribution. Interestingly, PVC-*g*-PBA showed a trimodal distribution, indicating that some unreacted PVC homopolymer remained.

To tune the T_g values for a multitude of applications, the amount of plasticizer was reduced by using less acrylate. Two new graft copolymers (PVC-*g*-PBA-0.5, PVC-*g*-PBA-1.0; Table 3, entries 1 and 2) and their corresponding 2EEA analogues (entries 3 and 4) were made by using initial monomer/VC ratios of 0.5:1.0 and 1.0:1.0, respectively.
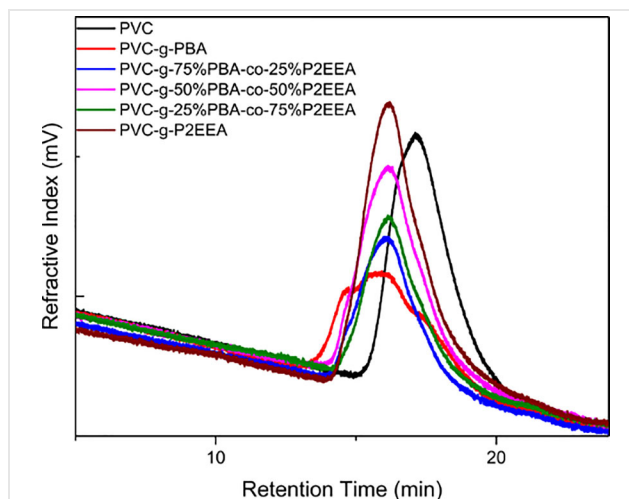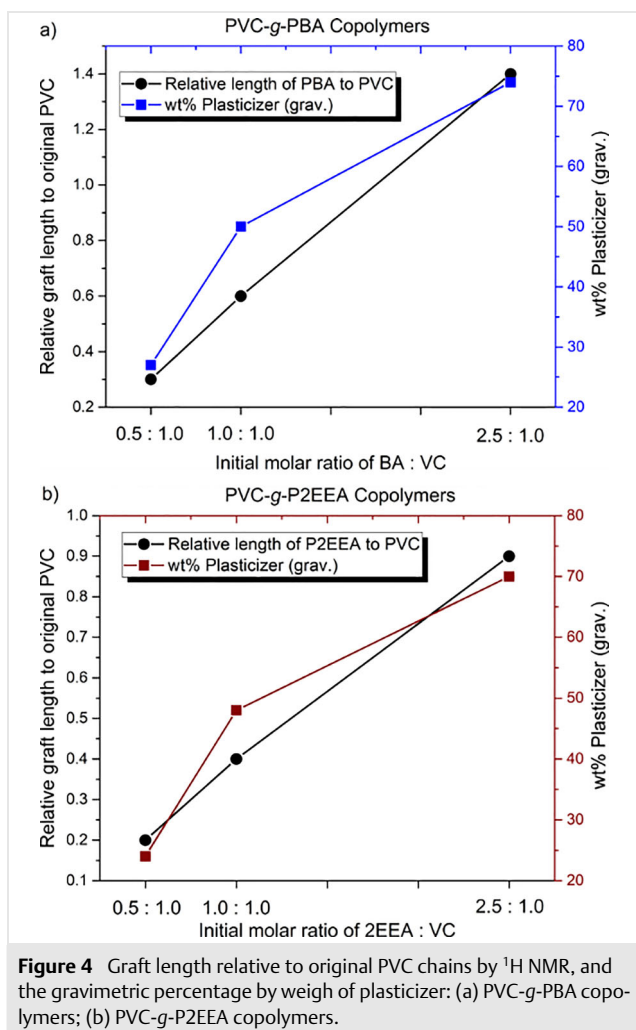
For polymers with PBA grafts, the PBA/PVC ratio increased almost linearly depending on the initial [BA]/[VC unit] monomer ratios (Figure 4a). The percentage by weight of plasticizer for PVC-*g*-PBA copolymers calculated by gravimetry ranged from 30 to 70%. A similar trend was seen for PVC-*g*-P2EEA copolymers, for which gravimetry indicated a broad range of mass percentages of the incorporated plasticizer (Figure 4b).

The T_g values of these PVC-*g*-PBA copolymers with reduced graft lengths are shown in Figure 5a. For the sample bearing the shortest PBA grafts, no distinct T_g value was detected, and this material did not feel flexible at room temperature. In comparison, for PVC-*g*-PBA-1.0 (T_g = –14 °C) and PVC-*g*-PBA-2.5 (T_g = –25 °C), there was a clear decrease in the T_g with increasing length of the graft polymer chains. PVC-*g*-PBA-1.0 contained 50% of plasticizer, and was clearly flexible when handled. For the PVC-*g*-P2EEA graft copolymers (Figure 5b), PVC-*g*-P2EEA-2.5 containing 70% plasticizer showed the lowest T_g (–47 °C). PVC-*g*-P2EEA-0.5 with 24% plasticizer had a T_g of 54 °C, and the material was rigid at room temperature. Surprisingly, when the amount of

Figure 4 Graft length relative to original PVC chains by ¹H NMR, and the gravimetric percentage by weigh of plasticizer: (a) PVC-*g*-PBA copolymers; (b) PVC-*g*-P2EEA copolymers.

Figure 5 DSC (second heating cycle) of (a) PVC-*g*-PBA graft copolymers and (b) PVC-*g*-P2EEA graft copolymers

polyether grafts was doubled to 48% in PVC-*g*-P2EEA-1.0, a T_g value of −41 °C was observed. For all six examples, the most cost-effective acrylate monomer-to-VC unit molar ratio was 1.0:1.0. Comparison of the PBA and P2EEA grafts at similar plasticizer contents shows a superior efficiency of the polyether compared with the butyl ester grafts.

Thermal stabilities of both the PVC-*g*-PBA and PVC-*g*-P2EEA copolymers were higher than that of unmodified PVC, as expected (SI; Figure S5 and Table S6). The thermal stabilities increase with increasing acrylate graft chain length.

The GPC traces of these PVC-*g*-PBA and PVC-*g*-P2EEA graft copolymers (SI; Figure S6 and Table S7) again showed shorter retention times than that of unmodified PVC, reflecting their higher effective volumes. For some samples, bimodal and trimodal distributions were observed, indicating that some unreacted PVC homopolymer remained. In some cases, the number-average molar masses of the graft copolymers were apparently smaller than that of unmodified PVC, which might be a reflection of the smaller hydrodynamic volumes of the graft copolymers compared with those of the linear polymers.
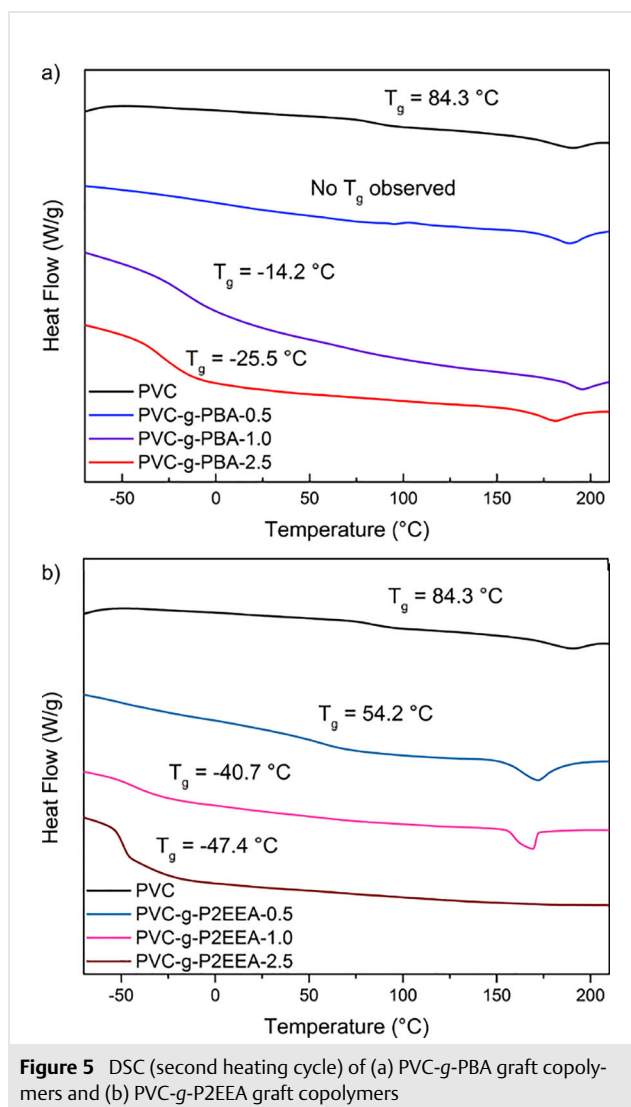
In summary, nine internally plasticized PVC graft copolymers were prepared from PVC by ATRP in one step, resulting in varying amount of appended polyacrylate plasticizers ranging from 24 to 75%. A wide range of T_g values (−54 °C to +54 °C) was observed. The most flexible graft copolymer was PVC-*g*-25%PBA-*co*-75%P2EEA, made with an acrylate monomer/VC unit molar ratio of 2.5:1.0. Graft copolymers with 50 wt% or more of plasticizer exhibited T_g values below 0 °C. The lower T_g values of P2EEA graft copolymers compared with PBA graft copolymers confirmed the higher plasticization efficiencies of polyethers compared with butyl ester grafts. Furthermore, the detection of a single T_g value for these samples indicates miscibility of both PBA and P2EEA grafts with PVC. GPC confirmed that the graft copolymers had larger effective volumes than unmodified PVC. These internally plasticized PVC materials were also more thermally stable than unmodified PVC. The simplicity

of one-step PVC modification by ATRP makes this approach to nonmigratory plasticizers attractive to industry. This strategy for covalently attaching plasticizers to PVC should significantly improve the environmental footprint of PVC usage.

Funding Information

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610764.

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(36) **PVC-g-50%PBA-co-50%P2EEA (Table 1, Entry 5); Typical Procedure**
A 10 mL Schlenk flask was charged with PVC (500.7 mg, 8.011 mmol) and DMF (3 mL), and the mixture was stirred and slightly warmed to fully dissolve the polymer. BA (1.43 mL, 9.97 mmol) and 2EEA (1.85 mL, 9.99 mmol) were then added to the solution. A 2 mL vial was charged with CuBr (34.22 mg, 0.2386 mmol) and 0.75 mL of DMF to form a suspension, which was transferred to the PVC solution by pipette. Residual CuBr was washed into the PVC solution with DMF (0.25 mL), and PMDETA (50 μL, 0.24 mmol) was added. The mixture was degassed by four freeze–pump–thaw cycles, then heated to 100 °C and stirred under N_2 for 2 h. An aliquot of the crude reaction mixture was taken and analyzed by ^{1}H NMR with $CDCl_3$ as solvent (conversion = 60 wt%). The polymer was precipitated by adding the mixture to MeOH (200 mL), followed by stirring for 30 min. The MeOH was decanted and the residual polymer was left overnight in additional MeOH (100 mL) without stirring. The solution phase was decanted and the polymer was dried under mild vacuum. The polymer, containing residual solvent, was washed with additional MeOH (5 mL), and the solvent was decanted. The product was thoroughly dried under vacuum to give a pale-green pliable polymer; yield: 1.5567 g (percentage wt. of plasticizer by gravimetry: 68%).
FTIR (neat): 2974 (m, alkane C–H), 2931 (m, alkane C–H), 2873 (m, alkane C–H), 1736 (s, ester C=O), 1169 (s, ester C–O), 1119 (m, ether C–O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.65–4.54 (br m), 4.54–4.38 (br m), 4.38–4.25 (br m), 4.25–4.12 (br m), 4.12–3.93 (br m), 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), 2.49–2.23 (br m), 2.23–1.97 (br m), 1.97–1.81 (br m), 1.74–1.57 (br m), 1.51–1.43 (br m), 1.43–1.29 (br m), 1.21 (t, J = 7.0 Hz), 0.94 (t, J = 7.3 Hz). From ^{1}H NMR integration: (PBA + P2EEA)/PVC = 0.9:1.0; PBA/P2EEA = 1.0:1.0; plasticizer = 60 wt%.

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