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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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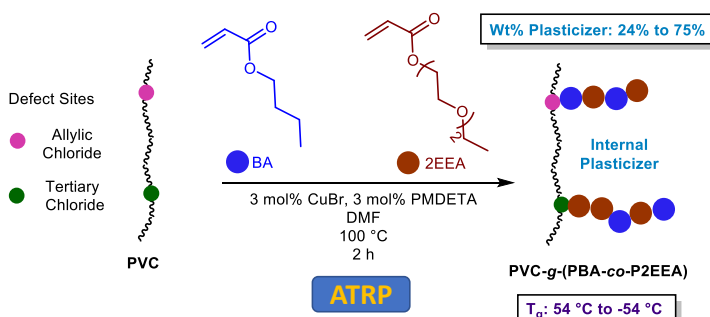
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Dedicated to Barry Trost: celebrating a lifetime of exploring the beauty of transition metal catalysis in organic synthesis.



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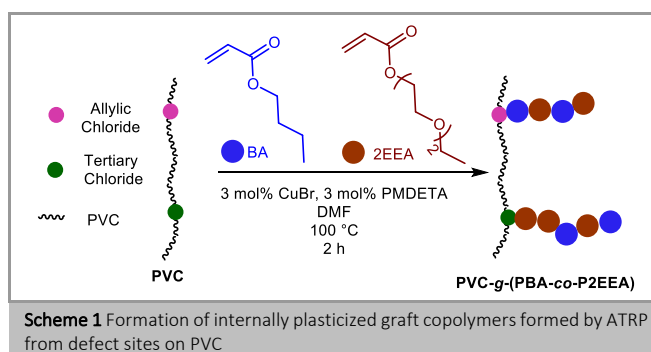
Abstract Internally plasticized PVC copolymers were grafted with butyl acrylate and 2-(2-ethoxyethoxy)ethyl acrylate using ATRP, resulting in well behaved polymers with a wide range of T_g values (-54 °C to 54 °C). When the grafted side chains made up more than 50% of the polymer by weight, the T_g values were below 0 °C. Covalent attachment of the plasticizing grafts uses one simple procedure starting with commercial PVC, making this strategy an industrially relevant and environmentally friendly alternative to the use of traditional small molecule plasticizers.

Key words Poly(vinyl chloride), PVC, ATRP, Internal plasticizer, Defect Sites

Poly(vinyl chloride) (PVC) is one of the most widely used thermoplastics. 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, and building materials.¹ Commonly used small molecule plasticizers such as phthalates can migrate out of the PVC matrix;² resulting not only in loss in mechanical properties but also to health issues 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 sulfide,^{3,4} amine,⁵ and azides (to form triazole linkages).^{6–16} Previous work in this lab highlighted the use of thermal azide/alkyne Huisgen cycloadditions to attach plasticizers to PVC.^{6,12,14,15} 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 with monomers bearing plasticizers has been accomplished as either block or random copolymers. Examples

include block copolymers of PVC with poly(*n*-butyl acrylate) (PBA)^{17,18} or poly(ϵ -caprolactone).¹⁹ In collaboration with Coehlo,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, a very attractive strategy is 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 Asgarzadeh²³ demonstrated the first application of copper-mediated ATRP initiated from these active sites, resulting in T_g values as low as -4 °C. We have recently demonstrated the use of acrylates in ATRP from PVC to prepare PVC graft copolymers 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 h, affording graft copolymers that were only partially soluble in THF, DMF, and NMP, likely due to crosslinking. In this paper, *soluble* internally plasticized PVC graft copolymers are prepared under improved conditions (**Scheme 1**). A variety of graft lengths are explored to generate graft copolymers with tunable flexibilities for a variety of applications.



In our previous study³⁵, a control experiment was performed in the absence of PVC, indicating that up to 23% homopolymerization occurred. To minimize both this competitive non-grafted polymerization as well as undesired crosslinking, the reaction duration was decreased from 24 h to 2 h. Control reactions were conducted without PVC for each monomer: BA and 2EEA (**Table 1, Samples 1 and 2**) using 3 mol% of CuBr, and 3 mol% of PMDETA in DMF at 100 °C. Nongrafted homopolymer was formed in only 10% for BA and 6% for 2EEA (**Table 1**), significantly lower than the 23% obtained after 24 h. A series of graft copolymers were then prepared (**Table 1, Sample 3 - 7**) using a 2 hour polymerization time.³⁶ Five different monomer ratios (BA : 2EEA) were investigated resulting in good conversions ranging from 56% to 78% (**Table 1, Samples 3 - 7**). More importantly, all these materials were soluble in CDCl₃, suggesting lack of cross-linking.

Table 1 Graft Polymerizations: Percent Conversion^a

Sample	[PVC]/[BA]/[2EEA]/[CuBr]/[PMDETA] ^b	%Conv. _{NMR} ^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%

^aAll polymerizations were conducted at 100 °C in DMF for 2 h; ^bInitial molar ratios; ^cConversion of total monomers

¹H 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. Two main trends were found: 1) the PBA : P2EEA ratio in the grafts were very close to the initial BA : 2EEA monomer ratio; and 2) PVC-*g*-PBA gave 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 percent conversions by ¹H NMR (**Table 1**) and by gravimetric yields (Supporting Information **Table S1**). Not surprisingly, the % conversions by ¹H NMR prior to work-up were higher than the gravimetric yields after work-up, due to loss of nongrafted polymer and general material loss. The work-up entailed precipitation of the crude polymer in MeOH. MeOH-soluble fractions were therefore lost. PVC-*g*-PBA shows closer values pre-work-up to post-work-up yields as nongrafted PBA is only partially soluble in MeOH, whereas the more polyether rich homo and graft copolymers are more likely to be washed away during the precipitation protocol from MeOH.

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

Sample	Initial molar ratio of [BA]/[2EEA]	Polymer molar ratio of PBA/P2EEA	Polymer molar ratio of (PBA + P2EEA)/PVC
3	BA only	PBA only	1.4 : 1.0
4	3 : 1	3.0 : 1.0	1.0 : 1.0
5	1 : 1	1.0 : 1.0	0.9 : 1.0
6	1 : 3	1.0 : 2.8	0.9 : 1.0
7	2EEA only	P2EEA only	0.9 : 1.0

The glass transition temperatures (T_g) 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 produced materials with very low T_g values compared to PVC ($T_g = 84$ °C) (**Figure 1**). Only a single T_g was observed, indicating that there is no microphase separation. The least depressed T_g was seen for PVC-*g*-PBA ($T_g = -25$ °C). 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 to those rich in BA. Some of the materials show melting temperatures (T_m) indicating these copolymers exhibit semicrystallinity, along with very low T_g values (Supporting Information **Table S4**).

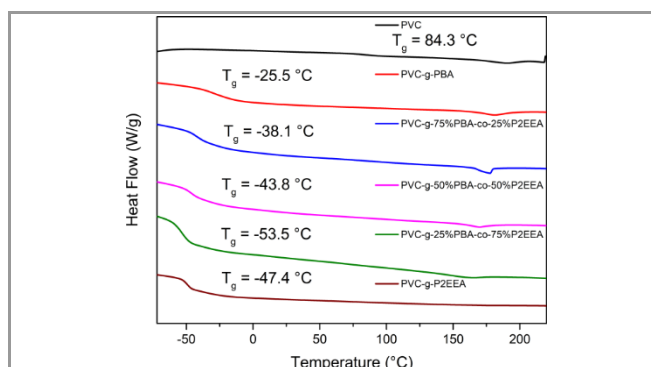


Figure 1 DSC (2nd heat cycle) of PVC graft copolymers made with a monomer to VC unit ratio = 2.5 : 1.0, *The slightly lower T_g value of PVC-*g*-25%PBA-*co*-75%P2EEA (wt% plasticizer_{grav.} = 68%) compared to PVC with full polyether grafts PVC-*g*-P2EEA (wt% plasticizer_{grav.} = 70%) is likely an artifact of the workup procedure, which preferentially dissolves 2EEA-rich copolymers.

Thermogravimetric analysis (TGA) (**Figure 2**) and Derivative Thermogravimetry (DTG) (Supporting Information **Figure S4** and **Table S2**) of these internally plasticized PVC materials were measured to examine their thermal stabilities. PVC and PVC bearing polyacrylate grafts exhibit two main stages of degradation. The onset temperatures of these modified PVC samples are higher than those of unmodified PVC, because the unstable allylic and tertiary chloride defect sites have been replaced with carbon grafts.³⁷ The thermal stabilities of the PBA and P2EEA grafts are similar.

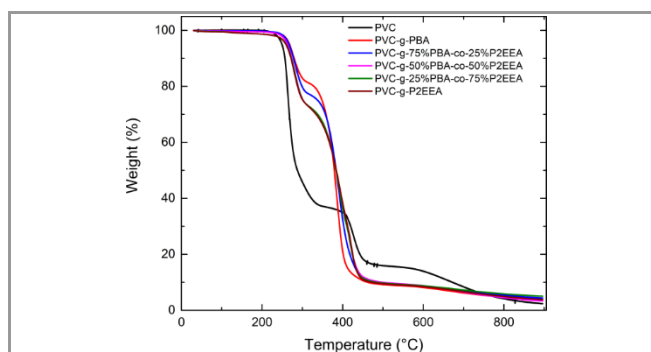


Figure 2 TGA curves of internally plasticized PVC samples made with a monomer to VC unit ratio = 2.5 : 1.0

The GPC traces of these PVC graft copolymers are shown in **Figure 3**. Compared to unmodified PVC, the retention times are shorter and the M_p , M_n , M_w , and M_z of the functionalized PVC samples are significantly larger compared to those of unmodified PVC (Supporting Information **Table S3**), reflecting their higher weights and effective volumes. Most of these new polymers have

a unimodal distribution. Interestingly, PVC-*g*-PBA shows a trimodal distribution, indicating that some unreacted PVC homopolymer remains.

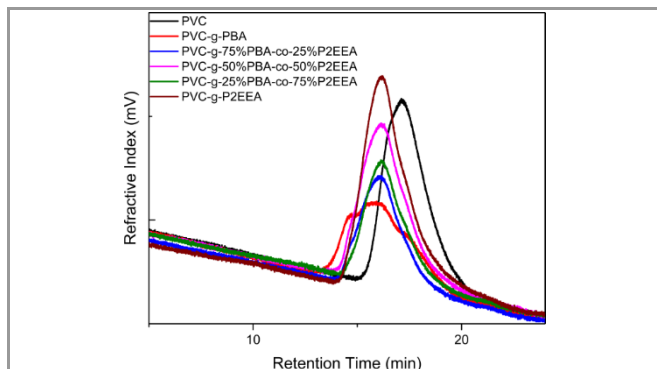


Figure 3 GPC traces of PVC Graft Copolymers (made with monomer to VC unit ratio = 2.5 : 1.0)

In order to be able 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) were made using initial BA : VC unit ratios of 0.5 : 1.0 and 1.0 : 1.0 (Table 3, Entries 1 - 2), as well as two 2EEA analogues (Table 3, Entries 3 - 4).

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

Entry	[PVC]/[BA]/[2EEA]/[CuBr]/[PMDETA] ^b	%Conv.-NMR ^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%

^aAll polymerizations were conducted at 100 °C in DMF for 2 h, ^bInitial ratios were calculated in mol; ^cConversion of total monomers

For polymers with PBA grafts, the PBA : PVC ratio increased almost linearly according to the initial [BA] : [VC unit] monomer ratios (Figure 4a). The wt% 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, wherein gravimetry indicated a broad range of wt% of incorporated plasticizer (Figure 4b).

The T_g values of these PVC-*g*-PBA reduced length graft copolymers are shown in Figure 5a. For the sample bearing the shortest PBA grafts, no distinct T_g value was detected. This material did not feel flexible at room temperature. By comparison, for PVC-*g*-PBA-1.0 (T_g = -14 °C) and PVC-*g*-PBA-2.5 (T_g = -25 °C), there is a clear decrease in T_g values with increasing length of the graft polymer chains. PVC-*g*-PBA-1.0 contains 50% of plasticizer and is 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 value (-47 °C) (Figure 4b). PVC-*g*-P2EEA-0.5 with 24% plasticizer resulted in a T_g value of 54 °C, meaning the material is rigid at room temperature. Surprisingly, when the amount of 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-efficient acrylate monomer to VC unit molar ratio was 1.0 : 1.0. Comparison of the PBA and P2EEA grafts at similar plasticizer content shows the

superior efficiency of the polyether compared to the butyl ester grafts.

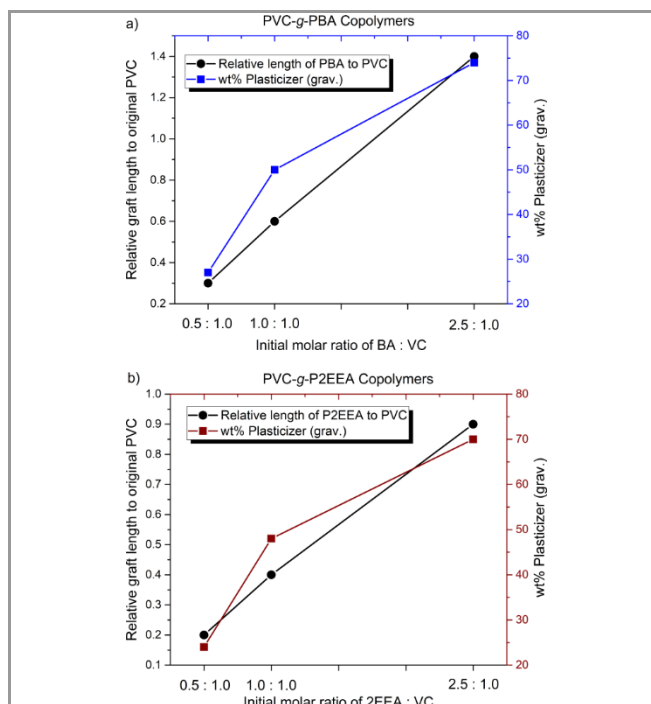


Figure 4 Graft length relative to original PVC chain by ¹H NMR and gravimetric wt% of plasticizer a) PVC-*g*-PBA copolymers; b) PVC-*g*-P2EEA copolymers

Thermal stabilities of both the PVC-*g*-PBA and PVC-*g*-P2EEA copolymers are higher than unmodified PVC, as expected (Supporting Information Figure S5 and Table S6). Thermal stabilities increase with increasing amounts of acrylate graft chain length.

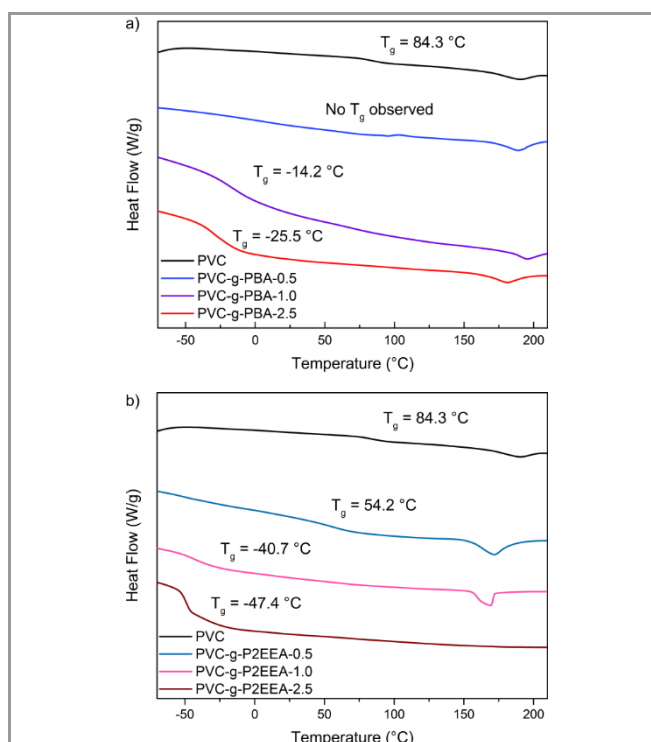


Figure 5 DSC (2nd heating cycle) of a) PVC-*g*-PBA Graft Copolymers and b) PVC-*g*-P2EEA Graft Copolymers

The GPC traces of these PVC-*g*-PBA and PVC-*g*-P2EEA graft copolymers (Supporting Information **Figure S6** and **Table S7**) again show shorter retention times than the unmodified PVC, reflecting their higher effective volumes. For some samples, bimodal and trimodal distributions are observed, indicating that some unreacted PVC homopolymer remains. In some cases, the M_n of graft copolymers are apparently smaller than that of unmodified PVC, which might be a reflection of the smaller hydrodynamic volumes of graft copolymers in contrast to 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 very wide range of T_g values (-54 °C to +54 °C) were observed. The most flexible graft copolymer is PVC-*g*-25%PBA-*co*-75%P2EEA made with a molar ratio of acrylate monomer : VC unit = 2.5 : 1.0. Graft copolymers with 50 wt% plasticizer or higher exhibit T_g values below 0 °C. The lower T_g values of P2EEA compared to PBA graft copolymers confirms the higher plasticization efficiencies of polyethers compared to 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 confirms larger effective volumes for these graft polymers compared to unmodified PVC. These internally plasticized PVC materials are more thermally stable compared to unmodified PVC. The simplicity of one-step PVC modification, by ATRP, makes this approach to non-migratory plasticizers very attractive to industry. This strategy to covalently attach plasticizers to PVC should significantly improve the environmental footprint of PVC usage.

Funding Information

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Supporting Information

YES (this text will be updated with links prior to publication)

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- (36) **Preparation of PVC-*g*-50%PBA-*co*-50%P2EEA (Table 1, Entry 5); Typical Procedure**
To a 10 mL Schlenk flask was added PVC (500.7 mg, 8.011 mmol) and DMF (3 mL). The mixture was stirred and slightly warmed to fully dissolve the PVC in DMF. BA (1.43 mL, 9.97 mmol) and 2EEA (1.85 mL, 9.99 mmol)

were added to the solution. To a 2 mL vial was added CuBr (34.22 mg, 0.2386 mmol) and 0.75 mL of DMF to form a suspension. The CuBr suspension was transferred to the PVC solution by pipet. Residual CuBr was washed into the PVC solution using 0.25 mL of DMF. PMDETA (50 μ L, 0.24 mmol) was added, and the reaction mixture was degassed via four cycles of freeze-pump-thaw, and then heated to 100 °C and stirred under nitrogen. After 2 h, an aliquot was taken to analyze the crude reaction by ^1H NMR using CDCl_3 as solvent (%CONV-NMR = 60%). The resulting polymer was precipitated by addition to 200 mL of MeOH, followed by stirring for 30 min. Then MeOH was decanted. The polymer was left in an additional 100 mL of MeOH overnight without stirring. The solution phase was decanted. The polymer was dried under mild house vacuum. The polymer (still containing residual solvent) was washed with an additional 5 mL of MeOH, and the solvent decanted. The product was thoroughly dried under

vacuum to yield 1.5567 g (wt% plasticizer_{grav.} = 68%) of a pale green, pliable polymer.

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). ^1H 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). Based by ^1H NMR integration: (PBA + P2EEA) : PVC = 0.9 : 1.0; PBA : P2EEA = 1.0 : 1.0; plasticizer_{NMR} = 60 wt%.

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