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Nitroxide mediated radical polymerization for the preparation of poly(vinyl chloride) grafted poly(acrylate) copolymers

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In view to control the thermal properties of PVC without the use of toxic phthalate derivatives, alkoxyamines were grafted onto an azide modified PVC, through copper catalyzed azide-alkyne cycloaddition (CuAAC), to initiate a radical polymerization of acrylate monomers including butyl acrylate (BA) and polyethylglycol acrylate (PEGA) monomers. A series of PVC-*g*-PBA copolymers having glass various temperature transition (T_g) between 63.5 to -10.5 °C were obtained. The PVC-*g*-PEGA copolymers presented a semi-crystalline behavior with a T_g of -4 °C and a T_m of 43 °C. This method, combining CuAAC click reaction and radical polymerization, was efficient to covalently link a plasticizing group on PVC. This “grafting from” strategy using alkoxyamine functionalized PVC can be expanded to produce new materials via nitroxide mediated polymerization of various monomers.

1. Introduction

With a global production of around 44 million tons/year, poly(vinyl chloride) PVC is one of the most industrially produced polymer in the world. While pure PVC is a highly rigid thermoplastic, its high tolerance to various plasticizers, lowering the glass transition temperature T_g of the material, allows to control its flexibility and ductility for a wide range of applications.¹⁻²

Usually plasticizers are introduced during the extrusion of the polymer. However, not covalently linked to the polymer, plasticizers can migrate outside the material over time, leading to contamination of the environment and loss of material properties.

For a long time, phthalate plasticizers were mostly used as additives to tune the PVC properties. But, for many of them, a high toxicity has been clearly established, and they were classified as carcinogenic, mutagenic or toxic to reproduction CMR products.³⁻⁸ In particular, the most used one, di-2-ethylhexylphthalate DEHP, causes endocrine disruption with dramatic consequences for the development of children.⁹⁻¹⁰

While they are progressively banned for sensitive applications, and the use of bio-sourced and non-toxic plasticizers is currently in progress,¹¹⁻¹⁵ phthalates are still expected to represent around 80% of the global plasticizer demand in 2022.¹⁶ However the safest plasticizers are still able to leach, reducing the lifespan of products.

PVC business is increasingly challenging high-performance and sustainable applications for demanding markets such as medical, building and construction, or automotive, and the covalent grafting of plasticizers is an efficient and elegant way to prevent the plasticizer migration,^{1, 17-18} affording even more safe and robust flexible PVC materials.

Different methods to functionalize PVC have been explored.^{17, 19-20} One way consisted in the substitution of a chloride atom of the PVC chain²¹ in order to graft a pendant group. Following this strategy, Michel et al. and Reineke et al. developed the grafting of thiolate group bearing phthalate derivatives and produced PVC with tunable T_g .²²⁻²⁴ Similarly, the PVC grafting of various groups, such as poly(styrene),²⁵ lauraldehyde-derived Mannich base,²⁶ cardanol alkyl ether,²⁷ Dehydroabiatic group,²⁸ via a pending amine group or epoxidized aliphatic methyl ester²⁹ has been explored to tune the properties of the polymer.

Otherwise, the introduction of azide groups via the Cl substitution of PVC can be a first step to the grafting of pending functions.^{20, 30-31} Then the copper catalyzed azide-alkyne cycloaddition (CuAAC) of alkynyl groups allowed the introduction of plasticizers including phthalate derivatives,³²⁻³³ cardanol³⁴ or polyglycerol.³⁵

Other strategies based on “grafting from” methods have been explored to initiate a polymerization process from the PVC chain. Atom transfer radical polymerization³⁶ is an attractive method to prepare functionalized PVC regarding the control of the polymerization of a wide range of monomers, and the reactive chloride atom of the PVC could be potential initiators since the dormant ATRP species is based on an activated carbon-halide site.³⁷⁻³⁸ As demonstrated by Percec et al., the PVC defects (allylic defects or chloride atom on tertiary carbon) present the best ATRP initiator sites.³⁹⁻⁴⁰ However the very low amount of reactive chloride atoms of the PVC toward ATRP activation limits the number of potential polymerization sites of the PVC backbone.⁴¹

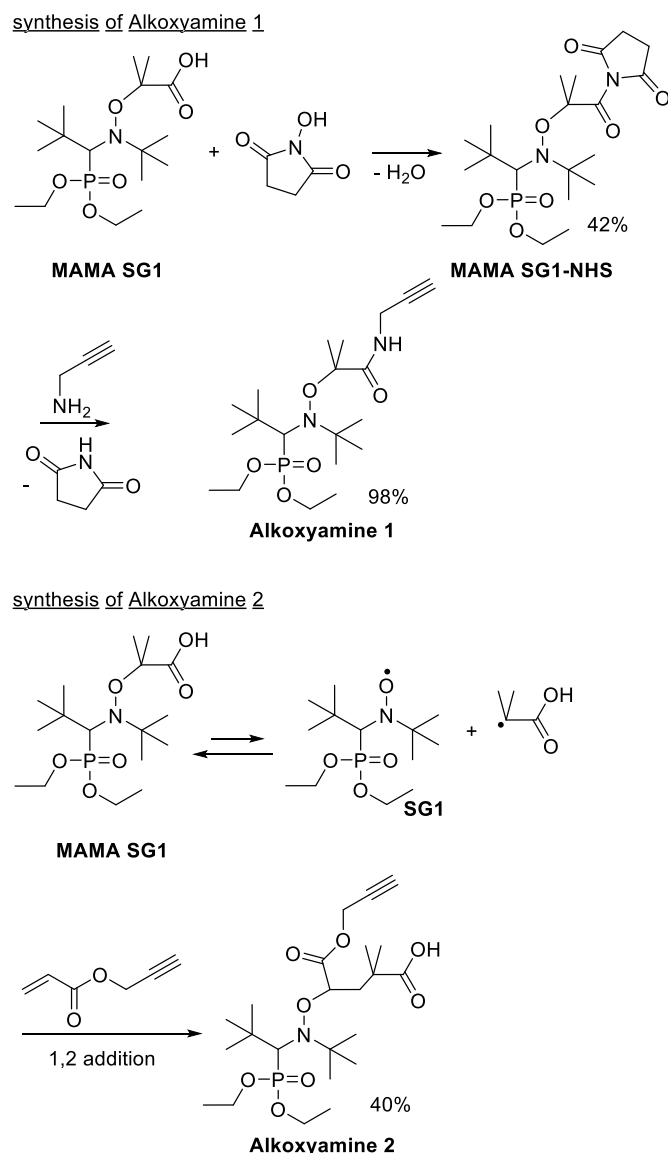


Fig. 1. Synthesis of alkoxyamines 1 and 2.

Despite this strong limitation, the modification of PVC materials was achieved via ATRP with various monomers.^{37, 42-50} In contrast, the radical polymerization from reversible addition fragmentation chain-transfer RAFT agents grafted on PVC remains confidential.⁵¹

Nitroxide mediated polymerization NMP is an efficient reversible-deactivation radical polymerization RDRP method for macromolecular engineering.⁵²⁻⁵⁴ In contrast to ATRP or RAFT, NMP does not require a metal catalyst or sulfur compound, which is a strong advantage to produce safe plastics. Entezami et al. used harsh conditions combining Friedel-Crafts, bromination and nucleophilic substitution reactions to graft TEMPO on PVC and to initiate the styrene NMP from the modified chains.⁵⁵

Here, we choose to introduce SG1 alkoxyamines onto the PVC backbone to initiate a NMP process and to build pending polymer chains to tune the T_g of the graft PVC. Our strategy consists of (i) the controlled substitution of chloride atoms with azide functions, followed by (ii) the introduction of the alkoxyamine possessing an alkynyl group via CuAAC click chemistry and, finally, (iii) initiation of a radical polymerization of acrylate monomers.

2. Results and discussion

2.1. Alkoxyamine

The PVC properties were tuned by a “grafting from” polymerization of acrylate monomers via a grafted alkoxyamine on the polymer chain and the initiation of a NMP process. In this contribution, the linking of the alkoxyamines through a triazole group was achieved via a CuAAC click reaction between a pendant alkynyl group and a PVC-N₃ polymer.

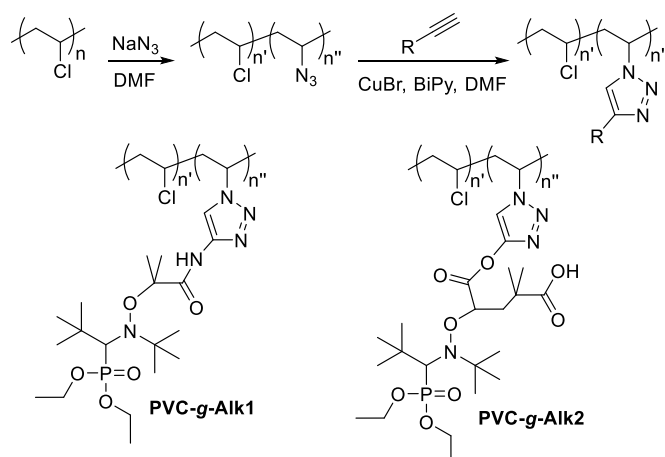


Fig 2. Synthesis of PVC-Alk1 and PVC-Alk2.

Here, we focus on nitroxide SG1 which is a versatile NMP controlling agent.^{52, 56-57} In particular, the BlocBuilder™ alkoxyamine or MAMA-SG1,⁵⁸ resulting from the trapping of a 2-methyl-propionic acid radical with SG1, is a highly efficient polymerization initiator.

Firstly, we chose to exploit the terminal acid group of MAMA-SG1 to introduce an alkynyl group. Following the literature, we first performed the reaction of hydroxysuccinimide on MAMA-SG1 to modify the terminal acid group into a N-acetoxy-succinimide function and then the resulting MAMASG1-NHS was reacted with propargyl amine to yield the alkoxyamine 1 (Fig. 1). The alkoxyamine 1 was fully characterized by ¹H and ¹³C NMR (Figures S2-S6), mass spectrometry and IR (Figure S7).

Another strategy to introduce the alkynyl group consisted of a 1,2 intermolecular radical addition (IRA) of MAMA-SG1⁵⁹ onto a propargyl acrylate (Fig. 1). Under thermal activation, MAMA-SG1 liberated the 2-methyl-propionic acid radical which reacted on the double bond of the propargyl acrylate and the resulting radical was trapped with SG1, leading to alkoxyamine 2 (Fig. 1). The alkoxyamine 2 was fully characterized by ¹H and ¹³C NMR (Figures S8-S9), mass spectrometry and IR (see below). In addition, the activation energy (*E_a*) of the C-O bond homolysis⁶⁰ of alkoxyamine 2 was evaluated to 117 kJ/mol by electron spin resonance (ESR) spectroscopy at 80 °C in *tert*-butyl benzene (see SI).

2.2. PVC-N₃

The azide substitution on a chloride atom of the PVC units is a well-known technique to introduce functionalities via copper catalyzed azide-alkyne cycloaddition (CuAAC) click reactions.²⁰ However, a fine control of the concentration of azide groups on the PVC chains is a dramatic issue since this parameter directs the number of functionalities on the graft polymer.

In this contribution, we utilized a PVC provided by Aldrich (*M_w* = 43000 g/mol and *M_n* = 22000 g/mol, according to Aldrich). PVC and sodium azide (PVC/NaN₃ wt-ratio of 1/1) reacted in DMF at 50 or 60 °C for 0.33-16.5 h (Table S1). The introduction of the azide groups on the PVC was confirmed by ¹H NMR (Figure S10) and IR with N₃ characteristic strong signal³² at around 2100 cm⁻¹. The presence of -Cl group on PVC was confirmed with the C-Cl stretching signal at 610 cm⁻¹ (see IR spectrum below).⁶¹ The concentrations of azide modified monomeric units were determined by elemental analysis (Table S1).

At 60 °C in DMF, between 4.4% and 43% of the -(CH₂-CHCl)- units were converted into -(CH₂-CHN₃)- units, depending on the reaction time and temperature (Table 1). The concentration of grafted N₃ increased with reaction time. However, when reactions longer than 6 h were performed, we did not observe a significant increase of grafted N₃ and a plateau of around 40% of modified PVC units was reached (Figure S11). Under very similar conditions, Chung, Kwak et al. reported a degree of azidation of 3.6%,³⁵ close to our results. Similarly, Braslau et al. reported a degree of azidation of 15% for a reaction time of 2.5 h at 62 °C in DMF.³² The Cl substitution with N₃ would depend on the PVC structure (molar weight, number of defects, etc).⁶²

To reduce the number of chloride substitution with the azide group, the reaction was performed at 50 °C and 1.4% and 3.4% of the PVC units were functionalized after 20 min and 1 h, respectively (Table 1).

Analyzed by SEC, the PVC containing 4.4% of azide monomeric units presented very similar molar weight and dispersity (*M_w* = 65700 g/mol, *Đ* = 2.0, SEC analyses using PS standard) to those of starting PVC, showing that the grafting of azide groups did not affect the structure of the PVC.

2.3. Grafting of alkoxyamine *via* click reaction

The grafting of alkoxyamine 1 on PVC-N₃ (containing 4.4% of N₃ units, see SI) was performed via a CuAAC click reaction (Fig. 2) in DMF at 30 °C for 24 h using CuBr/bipyridine as catalyst. ATR-IR analysis (Figure S12) of the resulting polymer confirmed the disappearance of N₃ signal and the presence of -C=N signals at 1650 cm⁻¹, attributed to the conversion of azide into triazole, and

the presence of amide signals (1760 cm^{-1}) and diethylphosphonate signals (1034 , 1010 and 958 cm^{-1}) of the alkoxyamine 1. However, the modified polymer was almost insoluble in organic solvent (CDCl_3 , THF, DMF, DMSO).

Table 1. Concentration of azide grafted on PVC.

entry	Time [h]	Temperature ($^{\circ}\text{C}$)	% of N_3 unit ^{a)}
1 ^{c)}	1	60	4.4
2	1	60	4.7
3	2.75	60	18
4	4	60	27
5	5.5	60	38
6	8.25	60	32
7	11	60	44
8	16.5	60	33
9	0.33	50	1.4
10	1	50	3.4

Conditions: DMF, PVC/ NaN_3 wt-ratio of 1/1. ^{a)} % of Cl atom substituted by azide in PVC, determined by elemental analysis.

It might be possible that during the reaction, the grafting alkoxyamine could liberate the nitroxide via the NO-CMe_2 bond homolysis and made a radical coupling, leading to a cross-linked PVC insoluble in organic solvents. Furthermore, the use of polar solvents, such as DMF, dramatically decreases the bond dissociation energy of SG1 alkoxyamines,⁶³ which also supports the theory of the bond homolysis, leading to a cross-linked and insoluble PVC.

Under the same conditions, the alkoxyamine 2 was successfully grafted using a PVC-N_3 (Fig. 2) containing 4.7% of azide units (Table 1) and the resulting modified PVC bearing alkoxyamine 2 was soluble in DMF. Actually, alkoxyamine 2, having a NO-CH- bond, would have a higher bond dissociation energy for the C-O homolysis (estimated to 117 kJ/mol in *tert*-Butylbenzene) compared to alkoxyamines which present a nitroxide NO-CMe_2- bond (bond dissociation energy of MAMA-SG1 of 112.3 kJ/mol in *tert*-Butylbenzene).⁶⁴⁻⁶⁶ The broad dispersity ($\text{Đ} = 3.9$, see SI) of PVC-Alk2 would suggest minor cross-linking side reactions occurring by radical coupling. During the purification process, the use of an aqueous solution of EDTA was important to remove the residual copper catalysts.⁶⁷ The IR spectrum of the resulting material confirmed the consumption of azide groups (signals at 2100 cm^{-1}) and the presence of new signals at 1600 cm^{-1} attributed to the -C=N- bonds of triazole (Fig. 3). The presence of a broad signal at 1700 cm^{-1} and three signals at 1050 , 1020 and 920 cm^{-1} , attributed to -C=O of acrylate and the diethylphosphonate group of MAMA-SG1 respectively (Fig. 3), confirmed the grafting of alkoxyamine 2 on PVC. The ^1H NMR spectrum showed the presence of -CH_3 signals of grafted alkoxyamine 2 between 1.4 and 1.0 ppm of the PVC signals (-CHCl- broad signals between 4.6 and 3.9 ppm and -CH_2- broad signals between 2.5 and 1.9 ppm, Fig. 3). However, the -CH_2- signals of alkoxyamine 2 remained very weak on the modified polymer and not clearly identified. According to integrals of ^1H NMR spectrum and elemental analysis (Table S2), 3.8% of units were functionalized with an alkoxyamine (Fig. 4).

A second PVC-N_3 containing a low concentration of 1.4% of azide units (entry 10 table 1) was used to synthesize alkoxyamine-grafted PVC.

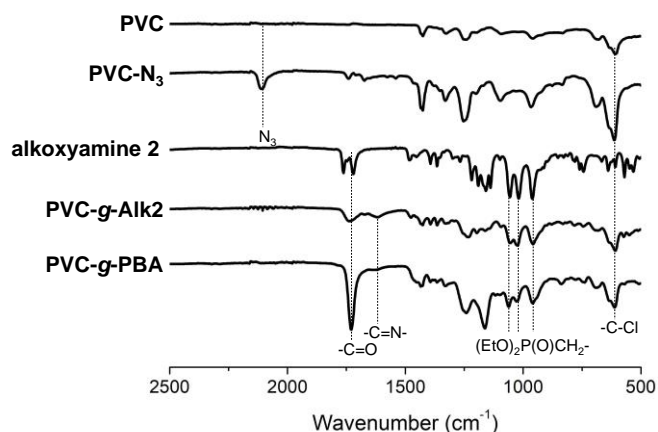


Fig. 3 ATR-IR spectra of PVC, PVC-N₃ (4.7%), alkoxyamine 2, PVC-g-Alk2 and PVC-g-PBA (91 wt% of BA, initiated from PVC-g-Alk2).

The IR spectrum confirmed the complete conversion of the azide sites and ¹H NMR and the oxygen concentration (Table S2), determined by elemental analysis, was in good agreement with a concentration of 1.4% of PVC units converted into a triazole.

2.4. Radical polymerization

Regarding its low *T_g* value of around -53 °C, poly(butyl acrylate) PBA is a prime candidate for graft PVC in view to prepare a migration-free soft material with tunable thermal properties.

Firstly, we evaluated the ability of alkoxyamine 2 to initiate the radical polymerization of BA. At 100 °C in DMF, the polymerization process showed an increase of molar masses with BA conversion with a conversion up to 85% of BA achieved after 6 h but the dispersity remained relatively high (*Đ* between 1.7 and 2.3, Table S3). The sudden increase of BA conversion was due to a hot spot consecutive to a gel effect observed between 2 and 4 h (Table S3).

Since alkoxyamine 2 proved to be an efficient BA polymerization initiator, we exploited the PVC-alkoxyamine 2 having 3.8% of pending alkoxyamine units to prepare ten PVC-g-PBA copolymers (Fig. 5) containing a wide range of BA concentration (Table 2). The polymerization was performed at 100 °C in DMF, using a BA/alkoxyamine ratio of 67/1. The reactions times were between 6 and 12 h and the BA conversions were measured by ¹H NMR from aliquots of the reaction media. BA conversions between 11% and 15% were achieved for a reaction time of 6 h, between 22% and 24% for 9 h, and up to 52% for 12 h (see SI table S4).

Under these reaction conditions, a series of ten PVC-g-PBA copolymers containing between 20-88 wt% of PBA (determined by ¹H NMR, Table 2) was prepared. The strong -C=O signal observed at 1720 cm⁻¹ on IR spectra of the copolymers confirmed the incorporation of BA monomers (Fig. 3). The IR spectra showed three signals at 1070, 1020 and 970 cm⁻¹ due to the presence of diethylphosphonate group of SG1 on the graft copolymers (Fig. 3). However, the presence of the nitroxide moiety was not clearly confirmed by ¹H NMR probably due to its too low concentration (Figure S13). The glass transition temperatures (*T_g*) of the grafted polymers were determined by DSC (see SI figures S14a-j) and a wide range of *T_g* values between 63.5 to -10.5 °C, for PBA concentration of 20 and 88 wt% respectively, was achieved (Table 2). As shown in Fig. 6, the concentration of grafted PBA had a strong effect on the *T_g* of the modified PVC. The decrease of *T_g* values seemed to be linearly affected by the increase of the weight

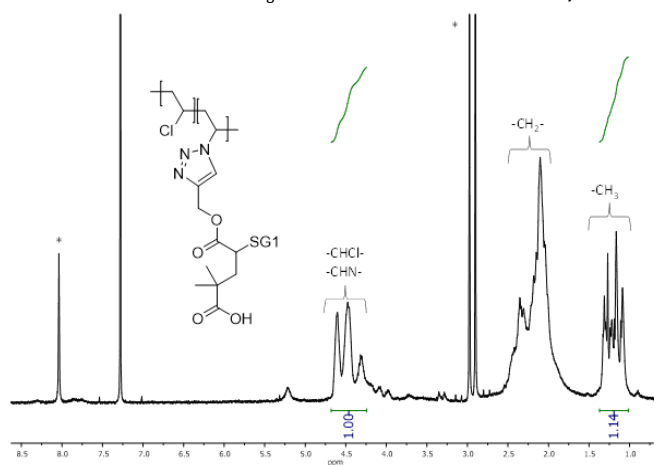


Fig. 4 ¹H NMR spectrum of PVC-Alk2 prepared from PVC-N₃4.7%, Table S2 (CDCl₃, 400 MHz, traces of DMF are marked with *).

of grafted BA but a shift to lower T_g values was observed when more than 50 wt% BA were achieved (Fig. 6). The lowest T_g value was $-10.5\text{ }^\circ\text{C}$ despite the high concentration of grafted BA (88 wt%).

Indeed, as reported by Braslau et al., triazole groups have an anti-plasticizing impact.⁶⁸

Table 2. Influence of BA concentration on T_g in PVC-*g*-PBA

entry	BA [wt%] ^{a)}	T_g [$^\circ\text{C}$] ^{b)}
1 ^{c)}	0	82
2	20	63.5
3	25	56
4	40	42
5	44	38
6	51	12.5
7	53	7.5
8	60	4.5
9	66	0.5
10	71	-1
11	88	-10.5

Conditions: $100\text{ }^\circ\text{C}$, BA/DMF ratio of 1/4, BA/alkoxyamine ratio of 67/1.^{a)} Determined by $^1\text{H NMR}$; ^{b)} determined by DCS; ^{c)} PVC provided by Aldrich

However, our PVC-*g*-PBA copolymers presented similar thermal properties that ones reported in the literature.

For instance, Chem et al. synthesized a PVC-*g*-PBA via BA ATRP initiation presenting a T_g value of $8.9\text{ }^\circ\text{C}$ with 58 mol% of PBA (74 wt% of PBA).⁶⁹ In contrast, Matyjaszewski et al. and Braslau et al. reported lower T_g values of -19 and $-25\text{ }^\circ\text{C}$, respectively, for a PVC-*g*-PBA obtained by ATRP and containing 80 wt% of PBA.^{41, 70} Additional parameters, such as the number of grafting sites or PVC chain length, would also affect the final properties of the functionalized PVC.¹⁷ Our strategy permitted to control the length of the grafted chains via NMP to provide a series of PVC-*g*-PBA copolymers having various T_g values.

Polyglycerol groups are efficient plasticizers of PVC.³⁵ We extrapolated our strategy to the polymerization of polyethylene glycol acrylate (PEGA) monomer initiated by alkoxyamine grafted on PVC. A monomethylether PEG acrylate having a molar weight of 2000 g/mol (PEGA-2000) was reacted with PVC-Alk2 and led to three different PVC-*g*-PEGA copolymers containing 17, 31, and 53 wt% of PEGA (determined by $^1\text{H NMR}$).

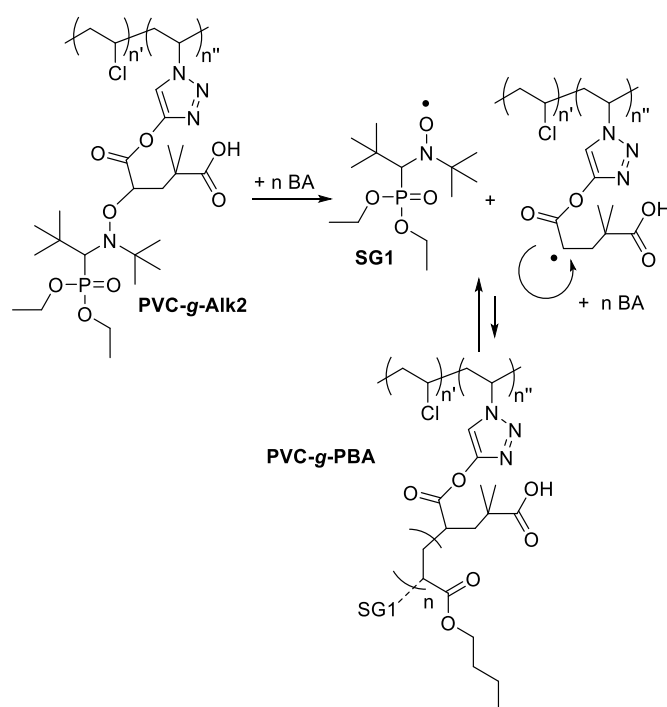


Fig. 5 Nitroxide mediated radical polymerization of BA initiated by PVC-Alk2

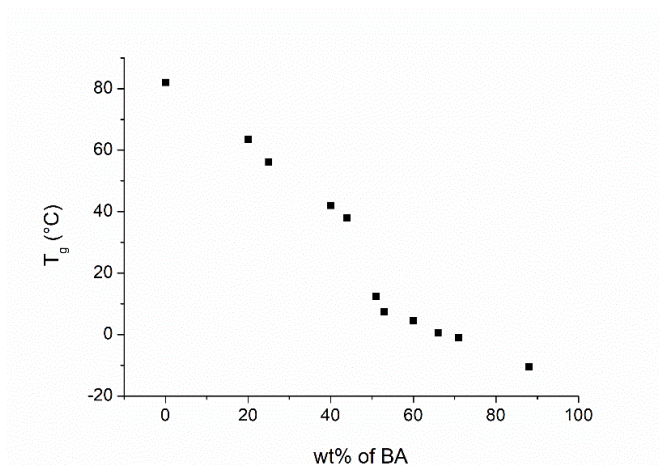
Table 3. Influence of the amount of grafted PEGA on T_g in PVC-*g*-PEGA

Entry	PEG wt%	T_g		T_m	
		Max E'' ^{a)}	Max $\tan \delta$ ^{a)}	Max $\tan \delta$ ^{a)}	T_m max ^{b)}
1	17	54 °C	67 °C	-	-
2	31	-4 °C	23 °C	43 °C	46 °C
3	53	-	-	41 °C	50 °C

^{a)} determine by DMA experiment; ^{b)} determined by DSC

The DSC analysis of the 17 wt% PVC-*g*-PEGA did not allow to determine indubitably the T_g of the graft polymer (Figure S15a). Thus, dynamic mechanical analysis (DMA) experiments were performed, revealing a glass transition around 60 °C (Max $E'' = 54$ °C, Max $\tan \delta = 67$ °C) (Figure S16b). As comparison, standard PVC exhibits a glass transition above 80 °C in the same condition (Max $E'' = 92$ °C, $\tan \delta = 98$ °C, Figure S16a). Interestingly, DMA of the copolymer containing 31 wt% of PEGA indicated a semi-crystalline behavior, with a glass transition at a lower temperature (max $E'' = -4$ °C, max $\tan \delta = 23$ °C) and a second transition around 40 °C (max $\tan \delta = 43$ °C Figure S16c). For the more PEGA enriched copolymers (53 wt% of PEGA) only a single transition around 40 °C (max $\tan \delta = 41$ °C, Figure S16d) is observed. The melting character of these transitions was confirmed for both products by DSC at respectively 50 °C and 52 °C (Figure S15 b and c) and is close to the T_m value of the PEG acrylate monomer (53 °C, see SI, Figure S1).

A low concentration of PEGA-2000 monomer allowed to decrease the glass transition temperature of the copolymer. Unfortunately, the crystallinity of the PEG chains dramatically limits this strategy, affording a crystalline behavior to the resulting copolymer.

**Fig. 6** Influence of BA concentration on T_g in PVC-*g*-PBA (Conditions: 100 °C, BA/DMF ratio of 1/4, BA/alkoxyamine ratio of 67/1; conversions determined by ^1H NMR; T_g determined by DSC).

3. Experimental

3.1. Materials

Chemicals and solvents were purchased from commercial sources (Aldrich, Acros, ABCR, TCI) and used without purification. PVC was provided by Aldrich ($M_n = 43000$ g/mol and $M_w = 22000$ g/mol according to Aldrich: $M_n = 30400$ g/mol, $\bar{D} = 2.1$ from THF-SEC analyses using PS standard). MAMA SG1-NHS was synthesized according to the literature (see SI).⁷¹

PEG-2000 acrylate (PEGA) was prepared according to the literature (see SI) using monoether-PEG and 2-Propenoyl chloride.⁷² ^1H NMR (400 MHz, CDCl_3 , Figure S1) δ 6.36 (d, $J = 17.3$ Hz, 1H), 6.09 (dd, $J = 17.3, 10.4$ Hz, 1H), 5.77 (d, $J = 10.4$ Hz, 1H), 4.25 (t, $J = 4.8$ Hz, 2H), 3.58 (m, $J = 5.5$ Hz, 178H), 3.31 (s, 3H); THF-SEC using PS standard: $M_n = 2700$ g/mol, $\bar{D} = 1.05$).

NMR spectra were recorded on Bruker AVL 300 or 400 (^1H -NMR 300.13 or 400.13, ^{13}C -NMR 75.46 or 100.60 and ^{31}P -NMR 121.4 and 161.9 MHz respectively) using CDCl_3 (reference: 7.26 ppm or 77.16 ppm) or $\text{DMSO}-d_6$ (2.50 ppm or 39.52 ppm) as solvent. Splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br m, broad multiplet. ^{13}C -NMR-ATP (attached proton test) sequence was applied to characterize the compounds. High resolution mass spectrometry (electrospray ESI-MS) was recorded at Spectropole-AMU (Marseille, France, see SI). FTIR spectra were recorded on an IR-ATR (Attenuated total reflectance IR) Perkin-Elmer spectrometer. Elemental analyses were purchased from ICSN CNRS laboratory (Gif-sur-Yvette, France) or Spectropole-AMU (Marseille, France, see SI). Temperature analysis (T_g , T_m) of the polymers were studied on a DSC Q20 (sequence: 5 min isotherm at $-50\text{ }^\circ\text{C}$, then $10\text{ }^\circ\text{C}/\text{min}$ temperature rate to $150\text{ }^\circ\text{C}$, sample mass: 8-15 mg). Values of T_g or T_m were determined from DSC thermograms using the universal V4.5A TA Instruments software. Dynamic mechanical analysis (DMA) experiments were performed at Westlake Catalyse on a PerkinElmer DMA 8000 apparatus, in torsion mode (1 Hz), between $-100\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$, at $3\text{ }^\circ\text{C}/\text{min}$. Polymer molecular weights were determined by THF-SEC using PSS EcoSEC equipped with RI detector: THF rate of $0.3\text{ mL}\cdot\text{min}^{-1}$ for sample ($0.15\text{ mL}\cdot\text{min}^{-1}$ pump ref), SEC columns: PL Resipore ($50 \times 4.6\text{ mm}$) and two columns PL Resipore ($250 \times 4.6\text{ mm}$) at $40\text{ }^\circ\text{C}$, sample concentrations of 0.25% in THF containing 0.25% of toluene as reference, injection volume of 20 μL . M_n (number average molecular weight), M_w (weight average molecular weight) and Đ (dispersity) were calculated with PS standard using PS-M Easivial (Agilent, USA).

3.2. Alkoxyamine synthesis

synthesis of Diethyl (1-(tert-butyl((2-methyl-1-oxo-1-(prop-2-yn-1-ylamino)propan-2-yl)oxy)amino)-2,2-dimethylpropyl)phosphonate (Alkoxyamine 1, Fig 1)

In a 500 mL two-necked round bottom flask, MAMA SG1-NHS (4.2 mmol, 1 equiv., 2.0 g) and 100 mL of dichloromethane were introduced and degassed under argon for 10 min. Then propargylamine (4.6 mmol, 1.1 equiv., 3 mL) was added dropwise under argon at $0\text{ }^\circ\text{C}$. After 4 h, the mixture was concentrated to around 10 mL under reduced pressure and 400 mL of pentane were added under argon. The mixture was placed at $5\text{ }^\circ\text{C}$ for 1 h and then filtered. The solution was evaporated under reduced pressure to yield the Alkoxyamine 1. ($m = 1.72\text{ g}$, yield = 98%)

^1H NMR (400 MHz, CDCl_3 , Figure S2) δ : 8.43 (s, 1H, NH), 4.14 (m, 5H, CH_2), 3.82 (ddd, $J=17.3, 4.3, 2.4$, 1H, CH_2), 3.34 (d, $J = 26.3\text{ Hz}$, 1H, CH-P), 2.12 (s, 1H, CH), 1.70 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.33 (dt, $J=16.3, 7.1$, 6H, $\text{CH}_3\text{-CH}_2$), 1.21 (s, 9 H, CH_3), 1.10 (s, 9H, CH_3).

^{13}C RMN (300 MHz, CDCl_3 , Figure S3) δ : 176.4 (C=O), 85.8 (C), 71.1-69.7 (d, $J=133.3\text{ Hz}$ CH), 71.0 (CH), 61.7 (CH_2), 60.0 (CH_2), 29.6 (CH_3), 29.3 (CH_3), 28.7 (CH_2), 27.0 (CH_3), 24.3 (CH_3), 16.5 (CH_3), 16.5 (CH_3). Additional NMR spectra: correlation spectroscopy COSY NMR (Figure S4), Heteronuclear Multiple-Quantum Correlation HMQC NMR (Figure S5), Heteronuclear Multiple Bond Correlation HMBC NMR (Figure S6). ATR-IR spectrum (Figure S7, cm^{-1}): 2980, 1667, 1515, 1368, 1222, 1142, 1053, 1022, 954, 743, 650, 596, 559. MS (ESI) calcd for $[\text{C}_{20}\text{H}_{40}\text{N}_2\text{O}_5\text{P}]^+ m/z = 419.267$; found 419.274 for $[\text{M}+\text{H}]^+$

synthesis of 4-((tert-butyl(1-(diethoxyphosphoryl)-2,2-dimethylpropyl) amino)oxy)-2,2-dimethyl-5-oxo-5-(prop-2-yn-1-yloxy)pentanoic acid (Alkoxyamine 2, Fig. 1)

In a 25 mL Schlenk, propargyl acrylate (10 mmol, 1 equiv., 1.1 g) and BlocBuilder™ MAMA SG1 (10 mmol, 1 equiv., 1.76 g) were dissolved in 8 mL of ethanol and degassed under argon for 30 min. The mixture was heated at $100\text{ }^\circ\text{C}$ for 1 h. After reaction, the mixture was transferred onto 80 mL of pentane and placed at $-15\text{ }^\circ\text{C}$ overnight. The resulting solid was filtered. ($m = 1.2\text{ g}$, $r = 40\%$)

^1H NMR: (400 MHz, CDCl_3 , Figure S8) δ : 4.56-4.73 (m, 5H), 3.95 (m, 5H), 3.69 (m, 1H), 3.26 (d, $J=21.59, 8.26\text{ Hz}$, 1H), 2.45-2.56 (m, 2H), 1.16 (s, 9H), 1.10 (s, 6H), 1.03 (s, 9H).

^{13}C NMR (CDCl_3 , 75,47 MHz, Figure S9) : 16.6 (dd, CH_3 , 1C) ; 23.5 (CH_3 , 1C) ; 28.0 (CH_3 , 1C) ; 28.2 (CH_3 , 3C) ; 30.0 (d, CH_3 , 3C) ; 30.0 (Cq, 1C) ; 40.4 (Cq, 1C) ; 41.2 (CH_2 , 1C) ; 52.0 (CH_2 , 1C) ; 41.2 (CH_2 , 1C) ; 59.4 (d, CH_2 , 1C) ; 62.0 (Cq, 1C) ; 62.4 (d, CH_2 , 1C) ; 68.9 (CH, 1C) ; 75.3 (CH, 1C) ; 77.2 (Cq, 1C) ; 83.2 (CH, 1C) ; 172.1 (Cq, 1C) ; 181.4 (Cq, 1C).

^{31}P NMR (CDCl_3): 24.4 ppm. HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{42}\text{NO}_8\text{P}]^+ m/z = 491.2648$; found 491.2648 for $[\text{M}]^+$. IR spectrum (see below).

3.3. Preparation of azide functional PVC (PVC- N_3)

Typical procedure for PVC- N_3 preparation: in a 250 mL round bottom flask, PVC (4 g) and NaN_3 (4 g) were mixed in 70 mL of DMF. The mixture was heated at 50 or $60\text{ }^\circ\text{C}$ for 0.33 to 16.5 h (Table 1). The mixture was filtered and then precipitated via a dropwise addition of the solution onto 400 mL of ethanol under high magnetic stirring. After filtration, the solid was dissolved in 100 mL of THF and precipitated in 400 mL of ethanol. The solid was dried under reduced pressure. The concentrations of grafted azide were determined by CHN elemental analysis (see table S1 and Figure S11).

^1H NMR (400 MHz, CDCl_3) δ : 4.6 - 4.15 (br m, 0.6H, $-\text{CHCl}$), 4.1-3.6 (br m, 0.4H, $-\text{CHN}_3$), 2.4 - 1.85 (br m, 1.2H, $-\text{CH}_2\text{CHCl}$), 1.85 - 1.6 (br m, 0.8H, $-\text{CH}_2\text{CHN}_3$) (the PVC- N_3 described contains 43% of N_3 units, see supporting information, Figure S10).

IR (cm^{-1}): 2910, 2108, 1426, 1331, 1254, 1098, 962, 655, 611 (see spectrum below).

3.4. Preparation of alkoxyamine functional PVC-alkoxyamine 2 (PVC-Alk2, Fig. 2)

In a 250 mL round bottom flask, **PVC-N₃** (0.16 mmol, 1 equiv., 1.0 g), and alkoxyamine **2** (0.8 mmol, 4 equiv., 400 mg), copper bromide (0.52 mmol, 3 equiv., 75 mg) and bipyridine (1.15 mmol, 7 equiv., 180 mg) were mixed in 100 mL of DMF and degassed under argon. The mixture let to react under argon for 24 h at RT. The solution was then precipitated in a mixture of 100 mL of ethanol and 300 mL of water in the presence of 150 mg of EDTA. The mixture was placed at -10 °C and the resulting solid was filtered, washed with acetone, and dried under reduced pressure. ($m = 1.129$ g, $r = 80\%$, $T_g = 75$ °C, $M_w = 65100$ g/mol, $\bar{D} = 3.9$)
¹H NMR: (400 MHz, CDCl₃, Fig. 4) δ : 4.46 (m, 1H, CHCl), 2.51 (m, 2H, CH₂), 1.20 (m, 1H, CH₃). PVC-Alk2 was analyzed by elemental analysis (Table S2).

3.5. Preparation of PVC-g-PBA

In a Schlenk flask under argon, PVC-Alk2 (1 equiv.) and butyl acrylate (67 equiv.) were mixed in DMF (volume ratio of DMF/BA of 4/1). The mixture was heated at 100 °C for 6 to 12 h (see SI). After reaction an aliquot of the reaction medium was analyzed by ¹H NMR to determine the BA conversion and the copolymer was precipitated via addition of 200 mL of ethanol or cold pentane (for high BA conversion polymerization). The resulting solid was filtered, washed with ethanol or pentane and dry under reduced pressure. The BA concentration in the copolymer was determined by ¹H NMR. Before DSC analysis, the polymer sample was dry for 4-8 h under vacuum to ensure the elimination of traces of DMF. ¹H NMR of the copolymers are presented in SI. ¹H NMR (400 MHz, CDCl₃, Figures S14a-j) δ : 4.8-3.5 (br m, overlapped signals of -CHCl-, -CHN- and -OCH₂- of PBA), 2.6-1.75 (br m, overlapped signals of -CHC(O) and -OCH₂-CH₂-, 3H), 1.75-1.1 (br m, overlapped signals of -CH₂-CH₂-, 4H), 1.0-0.7 (br m, -CH₃ of PBA, 3H).

3.6. Preparation of PVC-g-PEGA

In a Schlenk under argon, PVC-Alk2 (1.2 to 1.85 g, see SI) and PEG acrylate (0.71 to 1.60 g, see SI) were mixed in 15 mL of DMF. The mixture was heated at 100 °C for 18 h. After reaction an aliquot of the reaction medium was analyzed by ¹H NMR to determine the PEGA conversion and the copolymer was precipitated via addition of 300 mL of ethanol. The resulting solid was filtered, washed with ethanol and diethylether, dried under reduced pressure. The PEGA concentration in the copolymer was determined by ¹H NMR. Before DSC analysis, the polymer sample was dry for 4-8 h under vacuum to ensure the elimination of traces of DMF. ¹H NMR of the copolymers are presented in SI. ¹H NMR (300 MHz, DMSO, Figures S15a-c) δ 4.65 – 4.2 (br m, overlapped signals of -CHCl- and -CHN-), 3.65-3.45 (br s, OCH₂- signals of PEG), 3.25 (s, -CH₃), 2.6-2.0 (br m, overlapped signals of -CH₂-CHC(O)- and -CH₂-CHCl-).

Conclusions

A series of PVC-g-PBA and PVC-g-PEGA were synthesized via NMP initiated by alkoxyamines grafted on PVC chains. An alkyne function was introduced on MAMA-SG1 alkoxyamines via the modification of the terminal acid group into an alkyne amide group (alkoxyamine 1) or via the 1,2 intermolecular radical addition of an alkyne acrylate (alkoxyamine 2). The control of time and temperature of the reaction permitted to adjust the substitution degree of Cl atoms on PVC with azide groups, leading to PVC containing 1.4 to 44% azide units. Alkoxyamines 1 and 2 were grafted on the azide modified PVC via CuAAC reaction. The reaction with alkoxyamines 1 led to a very poorly soluble material, probably due to radical cross-linking reactions. The radical polymerization of BA initiated by PVC-Alk2 permitted to synthesize PVC-g-PBA copolymers having between 20 to 88 wt% of PBA and presenting a wide range of values between 63.5 to -10.5 °C. PEG-2000 acrylate was grafted to PVC (between 17 and 53 wt% of PEGA) using the same strategy and the DMA analysis revealed a semi-crystalline behavior and a low T_g of -4 °C and a T_m of 43 °C (31 wt% PEGA). Radical polymerization through grafted alkoxyamine on PVC is a strong strategy to covalently link a plasticizer on polymer chains and to finely tune its thermal properties without using toxic plasticizers, opening the way to safe soft materials with high permanence and durability. Eventually, this NMP “polymerization from” strategy could be extended to numerous different monomers to introduce various properties to PVC chains.

Author Contributions

AV, MD, and LA: Methodology, formal analysis, and investigation. CD and KL: Conceptualization, supervision, funding acquisition and Writing – original draft. DG: Conceptualization and validation. AK: Supervision, conceptualization, and Writing – review & editing.

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