

Synthesis of Low Molecular Weight Poly(vinyl acetate) and Its Application as Plasticizer

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ABSTRACT: Poly(vinyl acetate), PVAc, with a degree of polymerization $X_n = 10$ was prepared by chain-transfer radical polymerization using carbon tetrachloride and used as oligomeric plasticizer for commercial PVAc. However, the chlorinated chain ends cause a low thermal stability requiring mild Cl/H substitution. The product exhibits high thermal stability and excellent melt-compounding properties. Blends of oligomeric and commercial PVAc show single glass transition temperatures which decrease with higher oligomer content and exhibit small negative deviations from Fox' linear additivity rule. This indicates plasticization and miscibility being mainly due to entropic effects. Injection-moulded thick specimens show ductile behaviour at oligomer contents >10 wt %, while sheets with a thickness of 0.2–0.5 mm appear flexible already at 7.5 wt %. The oxygen permeability coefficients are an order of magnitude lower than those of low-density polyethylene. Due to the sum of their properties, the plasticized sheets present a promising alternative in the preparation of barrier materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40226.

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INTRODUCTION

An important, but rather neglected property of poly(vinyl acetate) is its low oxygen permeability coefficient of $P = 0.49$ barrer at 30°C (1 barrer = 10^{-11} cm³ (O₂) cm cm⁻² s⁻¹ mmHg⁻¹), which is six times smaller than that of low-density polyethylene (LDPE, $P = 2.93$ barrer at 25°C), a common packaging material.¹ Although poly(vinyl chloride) (PVC) with $P = 0.05$ barrer at 25°C or poly(vinyl alcohol) (PVA) with $P = 0.01$ barrer at 25°C exhibit better barrier properties,¹ a major advantage in using PVAc is its better thermoplastic processability since both PVC and PVA are known to start decomposing at their processing temperatures. However, pure PVAc is a brittle material and must be plasticized to improve its properties e.g. as a film.

Most of the relevant literature is concerned with the external plasticization of PVAc using low molecular weight, so called “monomeric” plasticizers as additives. Frequently used plasticizers are phthalates,^{2–7} phosphates,^{2,4} benzoates,^{4,6} and citrates.⁸ It is commonly accepted today that the plasticizer effect is caused by a weakening of the interactions between the polymer chains.^{9–11} This increases the chain mobility and causes an increase of the free volume. The mechanistic explanation con-

siders the interactions between plasticizer and polymer matrix and assumes that the molecules of the plasticizer are not permanently bound to the matrix, but can associate among each other.^{9,10,12} There is a dynamic exchange process wherein one plasticizer molecule attached to the polymer is readily replaced by another plasticizer molecule. At low plasticizer contents, the polymer–plasticizer interactions are dominant leading to an antiplasticization, whereas at higher plasticizer concentrations, plasticizer–plasticizer interactions become more significant.

A major point of concern with monomeric plasticizers in particular in packaging applications is the loss of the plasticizer due to migration, extraction, or evaporation.^{13–17} As a consequence, polymeric or oligomeric plasticizers became increasingly attractive in recent years because of the reduced loss due to their higher molecular weights.^{9,10,13,18–21} Widely used are polyethylene glycols (PEG) and polyesters. For PVAc, the use of polyesters, mixed with PVAc in emulsions is reported mainly for coatings and adhesives.^{22–27} But the miscibility between the plasticizer and the PVAc matrix as well as the plasticizer effect of the polyesters have not been investigated in detail. Moreover, the addition of polymeric plasticizers to PVAc by compounding could present an attractive way to prepare flexible PVAc

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Table I. Polymerizations of Vinyl Acetate Using Transfer Agents

Designation	Transfer agent AX	C_T	w (AX) %	Time ^a h	Yield %	M_n g mol ⁻¹	X_n	M_w/M_n
PVAc-D1	1-dodecanethiol ^b	0.33	36.2	4	37	21,160	245.9	1.6
PVAc-D2	1-dodecanethiol ^c	0.33	36.2	3	49	1,690	19.6	11.8
PVAc-F	fluorene	0.49	9.0	20	4	3,670	42.6	1.7
PVAc-C	CCl ₄	0.54	21.6	1	88	870 ^d	10.1	1.5

^aPolymerization time.^bSingle addition.^cContinuous addition.^dAfter subtraction of the molecular weight of CCl₄.

materials due to the compatibility with industrial processes, but was not examined until now.

Herein, we present an integrated study on the preparation of oligomeric poly(vinyl acetate) with a degree of polymerization (X_n) of 10 as well as its use as oligomeric plasticizer for commercial PVAc. Low molecular weight poly(vinyl acetate) was chosen as potential plasticizer due to its chemical constitution being identical to the commercial PVAc used as matrix, which promises a high miscibility of the two components as well as a good plasticization. Blends with commercial PVAc were prepared by melt compounding and the miscibility, the plasticizer effect, and permanence of the oligomer as well as the mechanical and rheological properties of the blends are reported. Finally, the oxygen permeability was assessed as a function of the plasticizer content.

EXPERIMENTAL

Telomerization of VAc Using Carbon Tetrachloride (CCl₄)

A 250-mL three-neck round-bottom flask with argon gas inlet, reflux condenser, and mechanical stirrer was charged with freshly distilled vinyl acetate (10 g, 0.12 mol), 2,2'-azobisisobutyronitrile (AIBN) (0.10 g, 0.61 mmol) and CCl₄ (2.78 g, 0.02 mol). The flask was purged at room temperature with argon for 15 min while stirring at a speed of 120 rpm, and then heated to 70°C with constant stirring under argon atmosphere for 60 min. Polymerization was interrupted by the addition of a small amount of hydroquinone and cooling to room temperature. The mixture was dried under vacuum at room temperature to constant weight to give a viscous, slightly yellow colored and tacky PVAc designated PVAc-C. Yield: 11.3 g (88 %). GPC: $M_n = 1020$ g mol⁻¹, $M_w = 1500$ g mol⁻¹.

Reduction of the Chlorinated PVAc

In a 250-mL three-neck round-bottom flask with gas inlet, reflux condenser and mechanical stirrer, PVAc-C (11.3 g, 0.01 mol) was dissolved in dried dimethyl sulfoxide (DMSO, 30 mL) at room temperature under argon atmosphere while stirring at a speed of 150 rpm. A solution of sodium borohydride (NaBH₄) (2.52 g, 0.07 mol) in DMSO (70 mL) was added. The mixture was heated to 50°C for 15 h with constant stirring under argon. The colourless reaction mixture was decanted from the solid precipitate and poured into cold phosphate buffer solution (600 mL) at pH 7.

The tacky precipitate was isolated by decanting the solvents, washed with water and dried under vacuum at 70°C to constant weight to give a viscous, tacky, and slightly yellow colored PVAc designated PVAc-R. Yield: 7.2 g (72%). GPC: $M_n = 910$ g mol⁻¹, $M_w = 1300$ g mol⁻¹.

Preparation of PVAc Blends

A DSM Xplore twin screw corotating microcompounder was used to prepare polymer blends of oligomeric PVAc-R and commercial PVAc. The extruder contains six individually controllable heating zones and two conical mixing screws with a length of 135 mm. The net volume is 15 mL. Polymers were simultaneously fed to the microcompounder through a hopper attached at the top of the barrel and melt-blended at 120°C with a screw speed of 100 rpm for 5 min under nitrogen. After that, the blends were transferred into a 12 mL removable injection nozzle of a DSM Xplore injection moulding machine at 120°C and injected into molds preheated to 30–40°C to produce plates with a diameter of 25 mm and a thickness of 1 mm used for rheological measurements as well as rectangular bars of 58 × 12 × 2 mm³ used for the three point flexural tests. Sheets were prepared using the DSM Xplore micro film device including a film die with a width of 35 mm and a thickness of 0.5 mm attached to the microcompounder.

RESULTS AND DISCUSSION

Oligomeric PVAc was chosen as plasticizer since it is, apart from the molecular weight, identical to the PVAc matrix. This promises a high miscibility of the two components as well as good plasticizing effects. For the target degree of polymerization, we arbitrarily aimed for $X_n = 10$. It is reported in literature that oligomeric PVAc with $X_n \approx 10$ can be synthesized by telomerization with chlorinated hydrocarbons such as carbon tetrachloride (CCl₄)^{28–33} or chloroform^{33,34} as telogens or by using transfer agents such as acetaldehyde,³⁵ methyl esters,³⁶ 1-dodecanethiol,^{37,38} aliphatic alcohols,^{39,40} 2-isopropoxy-ethanol⁴¹ or diethyl phosphite.⁴²

Synthesis of Thermally Stable PVAc Oligomers

Polymerization of VAc Using Transfer Agents. The oligomeric PVAc was synthesized by polymerization using transfer agents (Table I). Of all the substances used in literature, we limited the

screening to CCl_4 , 1-dodecanethiol, and fluorene (polymerizations using 1-dodecanethiol and fluorene are described in the Supporting Information). The chain transfer constants C_T were determined using the Mayo equation⁴³ (Table S1 and Figure S1 in the Supporting Information).

The transfer reactions using 1-dodecanethiol do not afford the target polymer despite a continuous addition of the transfer agent due to its low transfer constant ($C_T = 0.33$) requiring the addition of high amounts to the reaction mixture (Table I, Supporting Information Figure S2 and S3). Fluorene on the other hand is too little soluble in VAc to achieve $X_n = 10$ and slows down the polymerization resulting in a low yield of the product (Table I, Supporting Information Figure S4). Of the three transfer agents tested in this study, CCl_4 proved to be the most useful preparing oligomeric PVAc with $X_n = 10$. GPC analysis of PVAc-C using CCl_4 as transfer agent shows an excellent agreement of the calculated and obtained molecular weights (Table I, Supporting Information Figure S5) as well as a narrow molecular weight distribution ($M_w/M_n = 1.5$). The transfer constant of CCl_4 ($C_T = 0.54$) is approximately a half of a value previously reported in literature ($C_T = 0.96$ at 60°C).⁴⁴ The reason for this is unclear, but may be due to the use of a different radical starter. Due to the low X_n , the molecular mass of CCl_4 ($M = 153.82 \text{ g mol}^{-1}$) contributes significantly to the overall molecular weight of the polymer and needs to be considered in the calculation of X_n .

The presence of chlorinated oligomers in the form $\text{Cl}_3\text{C}-(\text{CH}_2\text{CH}(\text{OAc}))_n-\text{Cl}$ was confirmed by ESI-MS. The mass spectrum [Figure 1(a)] reveals oligomers in the range of $n = 4-21$ with the given values representing the monoisotopic masses plus sodium. The isotope patterns of the individual oligomers [Figure 1(c)] match the theoretical pattern [Figure 1(b), simulated using the software "Isotope pattern" of Bruker Daltonik] indicating a polymer chain with four chlorine atoms and are consistent with an ESI-MS measurement reported in the literature.⁴⁵

The weight loss determined by TGA under nitrogen indicates a two-step degradation mechanism [Figure 2(a)]. The first major step occurs from $100-390^\circ\text{C}$ followed by a second smaller one from $400-550^\circ\text{C}$. The mass loss associated with the first step is 77%, which is slightly more than the calculated elimination of all chlorine and acetate groups in the form of hydrogen chloride (HCl) and acetic acid (HOAc) based on the structure $\text{Cl}_3\text{C}-(\text{CH}_2\text{CH}(\text{OAc}))_{10}-\text{Cl}$.

FTIR spectra of the decomposition products recorded at 182°C [Figure 2(b)] and 235°C (Supporting Information Figure S6) in the first step clearly show the presence of HCl in the wavelength range of $\nu = 2600-3100 \text{ cm}^{-1}$ as evidenced by the rotational bands and the isotopic splitting. In addition, both spectra show C—O ($\nu = 1265 \text{ cm}^{-1}$, 1182 cm^{-1}), C=O ($\nu = 1775 \text{ cm}^{-1}$, 1797 cm^{-1}), and CH_3 umbrella ($\nu = 1384 \text{ cm}^{-1}$) bands indicating the elimination of acetic acid. The loss of HOAc resulting in the formation of a polyenic structure is characteristic for the first decomposition step of PVAc.⁴⁶⁻⁴⁸ In the present case, the decomposition presumably starts with the elimination of HCl since the bond energy of C—Cl (327 kJ mol^{-1}) is lower than

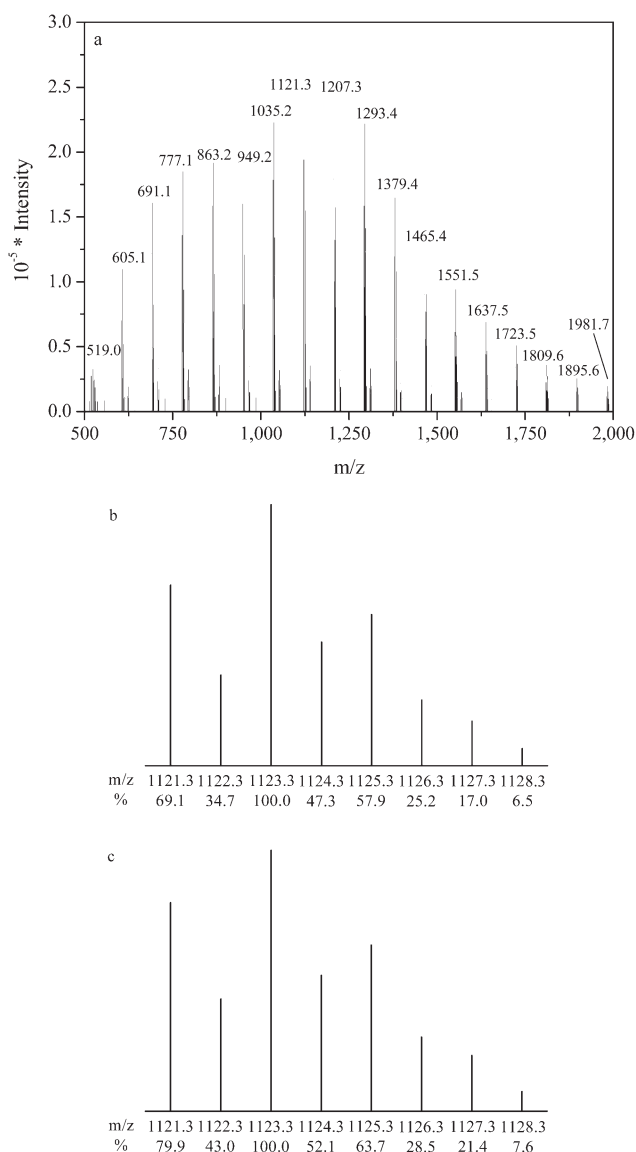


Figure 1. Mass spectrum of chlorinated PVAc-C ($m/z = 500-2000$) (a) and theoretical (b) as well as measured (c) isotope peak pattern of chlorinated PVAc oligomers with $X_n = 11$.

that of C—O (358 kJ mol^{-1}). This leads to the formation of double bonds, which facilitates the loss of adjacent acetate groups to form conjugated double bonds and finally results in a polyene. The FTIR spectrum recorded at 456°C [Figure 2(c)] in the second decomposition step does not show any signs of HCl, but traces of acetic acid are still visible. Thus, a small number of acetate groups seem to remain in the polymer backbone after the first step. In addition, traces of aromatic compounds can be observed in the IR spectrum indicating the decomposition of the polyenic structure formed by side chain elimination, i.e., of the polymer backbone.⁴⁶⁻⁴⁸ However, the low amounts of observed aromatic compounds and the high residual mass (16%) suggest an incomplete thermal degradation of PVAc-C.

Since oxygen is known to speed up the elimination of hydrogen chloride, preparation, handling, and storage of PVAc-C was done under argon. Nevertheless, the product had a

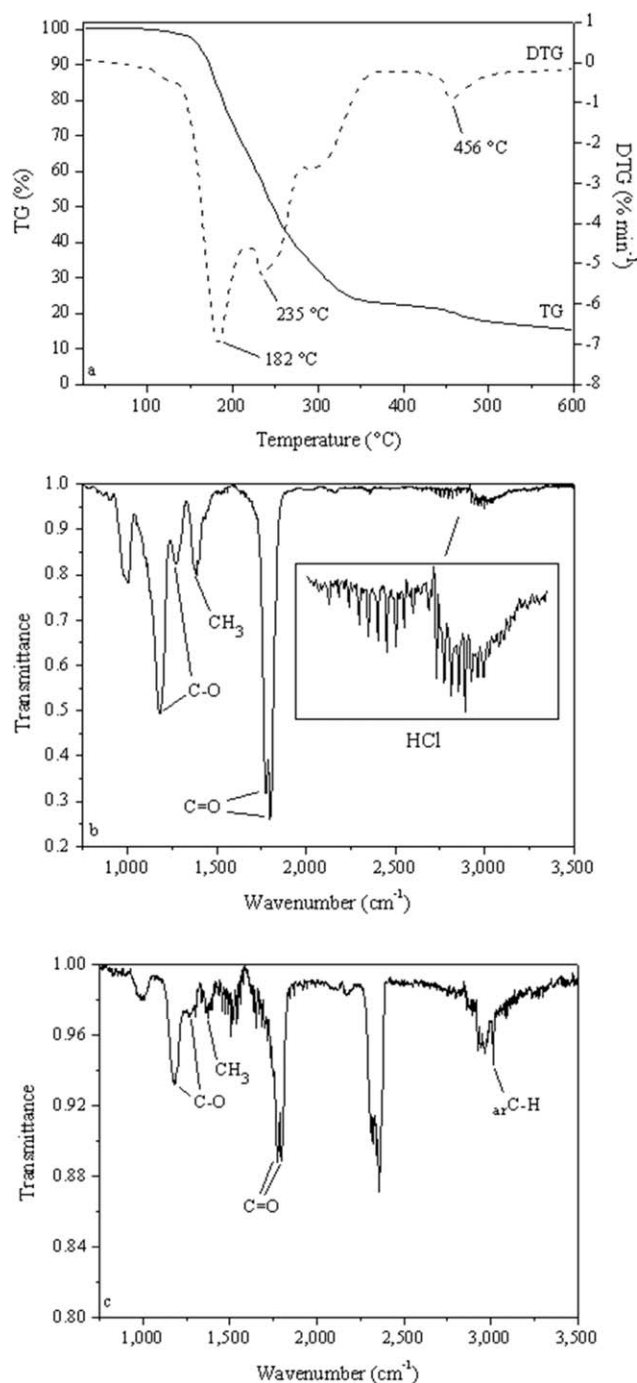


Figure 2. Thermal behavior of PVAc-C containing C–Cl end groups: mass loss (TG) and differentiated mass loss curve (DTG) determined by TGA (a) and FTIR spectra of the volatile components at 182°C (b) and at 456°C (c).

slightly yellow color after drying. Under atmospheric conditions, the originally viscous product turned black within 6 days, became increasingly liquid, and smelled of vinegar. Trying to blend PVAc-C with commercial PVAc-V resulted in a brown to black mass after several minutes despite working quickly at only 50°C and under inert gas. This is consistent with previous findings on chlorinated vinyl acetate oligomers.^{32,33,49,50}

Reduction of the Chlorinated PVAc. In order to improve the stability of PVAc-C, the C–Cl end groups were reduced using sodium borohydride in dry dimethyl sulfoxide. For this mild reduction, a 6:1 molar ratio of NaBH₄ to the original amount of carbon tetrachloride was used to ensure complete transformation of the chlorine end groups. In addition, the temperature was kept at 50°C to prevent an undesirable reduction of the acetate groups. The final reaction mixture exhibited a pH value of 10 and an unpleasant odor due to the reduction of dimethyl sulfoxide to dimethyl sulfide. To prevent major hydrolysis of the product, the polymer was precipitated from a cold phosphate buffer solution, keeping the pH constant at 7. Despite these efforts, the yields did not exceed 72% possibly due to inevitable hydrolysis during work up. GPC of the product designated PVAc-R shows a $M_n = 910 \text{ g mol}^{-1}$, which is close to the desired $X_n = 10$. The molecular weight distribution was similar to that of the starting material (Supporting Information Figure S7).

TGA measurement of PVAc-R shows a two-step degradation [Figure 3(a)] comparable to that of commercial PVAc.^{46,51} The first major step occurs from 240 to 390°C and the second smaller one from 400 to 550°C. That is, the onset of decomposition is increased by 140°C as a result of the chlorine end-

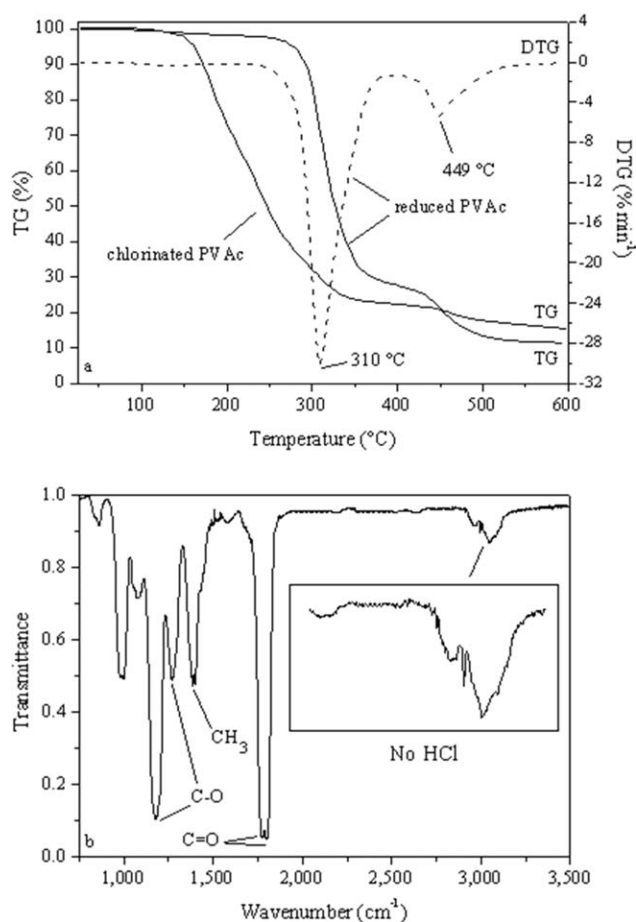


Figure 3. Thermal behavior of PVAc-R containing C–H end groups: (a) TG and DTG curve determined by TGA; the mass loss of PVAc-C [cf., Figure 1(a)] is included as reference. (b) FTIR spectrum of the volatile components at 310°C.

groups being replaced by hydrogen. The mass loss associated with the first step is 71%, which is in good agreement with the calculated total elimination of acetic acid based on the structure $\text{H}_3\text{C}-(\text{CH}_2\text{CH}(\text{OAc}))_{10}-\text{H}$. FTIR analysis of the volatile compounds in the first step at 310°C does not show signs of HCl indicating a high degree of chlorine substitution, but only CH_3 umbrella ($\nu = 1384\text{ cm}^{-1}$), $\text{C}=\text{O}$ ($\nu = 1775\text{ cm}^{-1}$, 1797 cm^{-1}), and $\text{C}-\text{O}$ ($\nu = 1271\text{ cm}^{-1}$, 1182 cm^{-1}) bands demonstrating deacetylation [Figure 3(b)], which results in the formation of a polyene. Similar to the chlorinated PVAc, the FTIR spectrum of the second step at 449°C also contains traces of acetic acid (Supporting Information Figure S8) as well as aromatic compounds and a rather high residual mass (11%) is found. Because of the reduction resulting in a drastic increase of the thermal stability, PVAc-R can be stored for prolonged periods under atmospheric conditions and does not lead to discolorations when compounded at elevated temperatures.

Plasticizing Effect of Oligomeric PVAc

Blend Characteristics. Melt compounding of commercial PVAc (weight average molecular weight $M_w = 50,000\text{ g mol}^{-1}$) and PVAc-R in a microcompounder afforded homogeneous blends, which were mostly colorless unless PVAc-R already showed a slight yellow discoloration. The blends are referred to as BX, where X is the concentration of PVAc-R in the blend. The 1 mm and 2 mm thick injection molded samples were slightly cloudy, whereas the sheets exhibiting a thickness of $200\text{--}500\text{ }\mu\text{m}$ appeared highly transparent. Generally, the samples became more flexible with increasing PVAc-R concentration proving the ability of PVAc-R to act as plasticizer for brittle, middle molecular weight PVAc. Samples with PVAc-R contents of $\geq 25\%$ (B25–B90) were too soft to be processed by injection molding.

Glass Transition Temperatures. The glass transition temperatures (T_g) of the blends were determined using DSC. Pure PVAc-V exhibits a T_g of 40.5°C (Supporting Information Table S2) consistent with the value of the supplier ($T_g = 40^\circ\text{C}$). Thus, PVAc-V appears hard and brittle at room temperature. In contrast, T_g of the oligomeric PVAc-R was -6.1°C corresponding to a viscous and tacky product.

Close examination of the DSC traces (Supporting Information Figure S9) reveals that all blends exhibit a single glass transition indicating that PVAc-V and oligomeric PVAc-R are miscible, respectively. The T_g values decrease with increasing weight fraction of PVAc-R demonstrating a plasticizer effect [Figure 4(a), markers]. Relating to the common explanation of plasticization as described in the introduction, this decrease of T_g is due to a reduction of the intermolecular interactions of PVAc-V caused by incorporation of the oligomeric PVAc-R molecules resulting in a facilitation of the chain mobility and consequently in an increase of the free volume.

Figure 4(a) also reveals that the glass transition temperatures of the blends show a negative deviation from Fox' linear additivity rule (dashed line)

$$\frac{1}{T_{g,\text{blend}}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where $T_{g,\text{blend}}$ is the glass temperature of the blend, and w_i and $T_{g,i}$ are the weight fractions and glass temperatures of the blend components ($i = 1$ denotes the T_g of PVAc-R). Deviations are due to the fact that Fox' additivity rule does not consider the thermodynamic changes of the blend components upon mixing.^{52–54} Rather, the T_g values of the miscible PVAc blends can be fitted successfully using the third order T_g vs. composition equation^{52,55}

$$\Delta T_g = T_{g,\text{blend}} - T_{g,\text{add.Fox}} = (T_{g,2} - T_{g,1}) \cdot [K_1 \cdot w_{2c} - (K_1 + K_2) \cdot w_{2c}^2 + K_2 \cdot w_{2c}^3] \quad (2)$$

based on considerations in the literature,^{52–58} which includes thermodynamic effects and where $T_{g,\text{blend}}$ is the measured glass temperature of the blend, $T_{g,\text{add.Fox}}$ is that of the blend calculated by the Fox equation, $T_{g,i}$ are the glass temperatures of the components ($i = 1$ denotes the T_g of PVAc-R) and $w_{2c} = (T_{g,\text{add.Fox}} - T_{g,1}) / (T_{g,2} - T_{g,1})$ is the corrected weight fraction of PVAc-V.

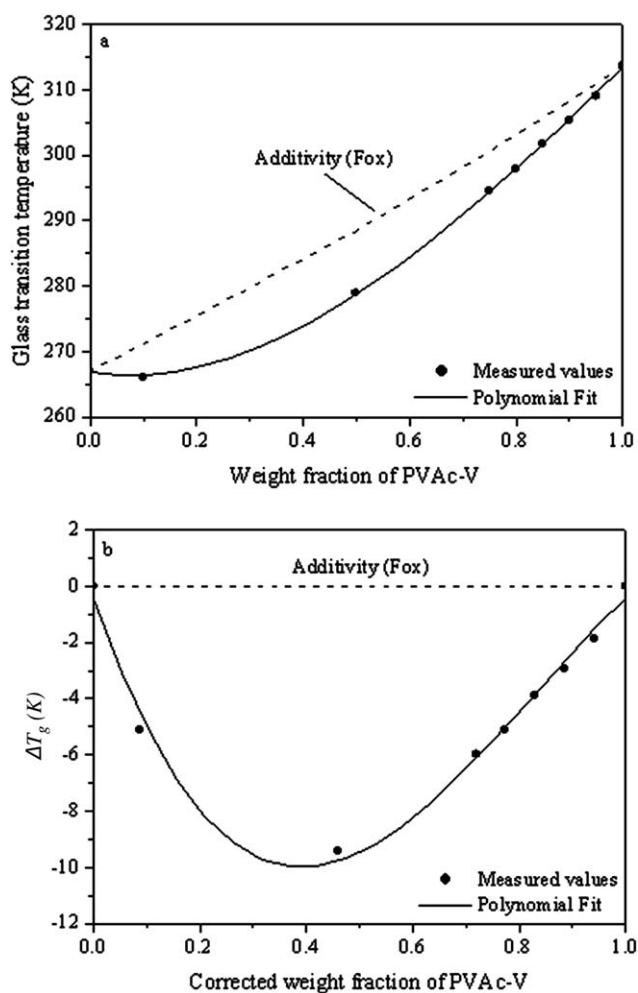


Figure 4. T_g values of the blends show a negative deviation from Fox' linear additivity rule (dashed lines) illustrated as (a) T_g vs. composition curve and (b) ΔT_g vs. composition curve.

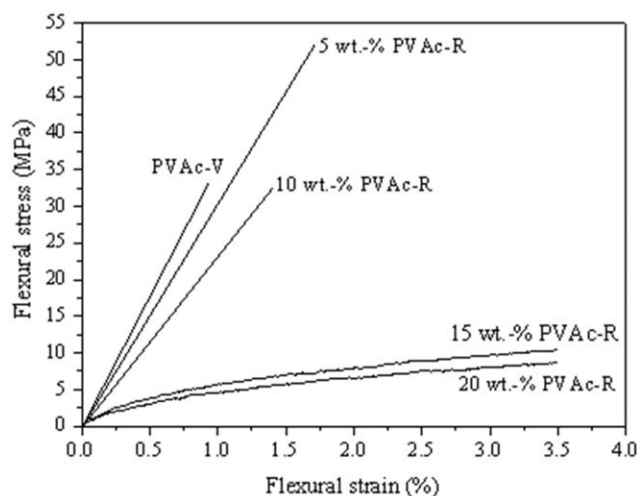


Figure 5. Flexural stress-flexural strain curves of PVAc-V mixed with different concentrations of oligomeric PVAc-R.

Plotting ΔT_g vs. w_{2c} [Figure 4(b), markers] and fitting eq. (2) to the data [Figure 4(b), continuous line] provides the fitting parameters $K_1 = -1.15$ and $K_2 = -0.77$, as well as a negative value for the difference $\Delta K = K_1 - K_2$. Both negative K_1 and ΔK confirm the negative deviation and are indicative of compatible blends with prevailing conformational entropic effects.^{54,56} Based on the literature,^{52–58} this is caused by a low probability of intermolecular interactions between polymer and plasticizer due to a low interaction energy. This results in a lower local orientation of polymer chains in the neighborhood of these interactions and, thus, an increase of induced conformational rearrangements. Consequently, the conformational entropy and free volume increases, whereas T_g decreases below additivity. Another effect is that the conformational entropy contribution to the polymer miscibility is increased. Hence, the miscibility of PVAc-V and PVAc-R is not attributed to the ultimate condition of strong interactions between the two species, which have to overcome the interactions acting within the individual components, but rather to predominant conformational entropy contributions to the mixing free energy.^{52,55,56}

The negative deviation observed in this study could be explained by the incorporation of the oligomeric PVAc molecules and thus by the plasticizer effect. Probably, the weakening of the interactions between the chain segments of the PVAc matrix causes a higher mobility and the prevailing entropic effects, as described in the literature.^{53,59} By comparing with investigations of other polymer-plasticizer-systems it can be concluded that the negative deviation seems to be indicative of a plasticization.^{59,60}

Mechanical Properties. The mechanical properties of the blends were examined using three point bending tests. Pure PVAc-V shows the expected hard-brittle behavior with ideal linear-elastic regime and low breaking strain (Figure 5; Supporting Information Table S2). The blends B5 and B10 exhibit similar hard-brittle behaviour albeit lower flexural moduli E_f . In contrast, the blends containing more than 15 wt % PVAc-R show ductile behavior and do not break during testing (Figure 5). The linear-elastic regime is rather small and characterized by an

approximately five times smaller flexural modulus than commercial PVAc. Beyond the proportionality limit, plastic deformation occurs. However, a true yield-point is not observed under the applied testing conditions. Thus, oligomer concentrations exceeding 15 wt % lead to flexible blends. Interestingly, the sheets already appear flexible at PVAc-R concentration exceeding 7.5 wt %.

The increasing flexibility is evident from the steady decrease of E_f with increasing oligomer content (Figure 6) due to plasticization. In addition, Figure 6 shows that E_f decreases slightly up to 10 wt % oligomer and then drops significantly from 10 to 15 wt % PVAc-R indicating the change from the hard-brittle to ductile behavior. This presumably indicates the presence of specific interactions between the blend components at low PVAc-R contents (cf. mechanistic theory of plasticization) causing a hindrance in segmental motion and thus, a reduction of the plasticizer effect. After that, the significant decrease of the mechanical properties could be due to an increased weakening of the interactions between the PVAc-V chains since the polymer-oligomer interactions are transient and the oligomer-oligomer interactions become more significant due to the higher oligomer contents. Despite this, a continuous plasticization of PVAc can be assumed since the T_g values show negative deviations from Fox over the full composition range.

Rheological Properties. For the investigation of the rheological properties, the viscosities of the blends were measured as a function of the shear rate. The rheological properties were determined at 80°C since the blends were too liquid at processing temperature (120°C) to ensure suitable and well-defined $\log \eta$ vs. $\log \dot{\gamma}$ curves. All samples show Newtonian behavior at low shear rates and shear thinning behavior at higher shear rates (Figure 7). The limiting values at low shear rates represent the zero-shear viscosity η_0 . The viscosity decreases with increasing shear rate due to a lowering of the interchain interactions resulting in a lower degree of entanglements and thus in a better orientation of the polymer chains parallel to the flow field.

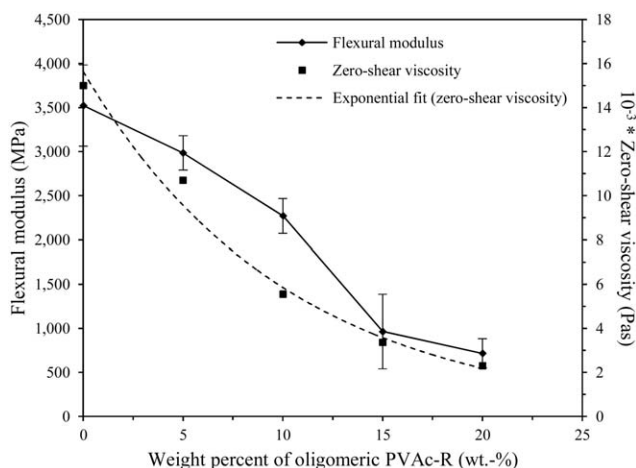


Figure 6. Zero-shear viscosities η_0 and flexural moduli E_f of the PVAc blends as a function of the PVAc-R concentration.

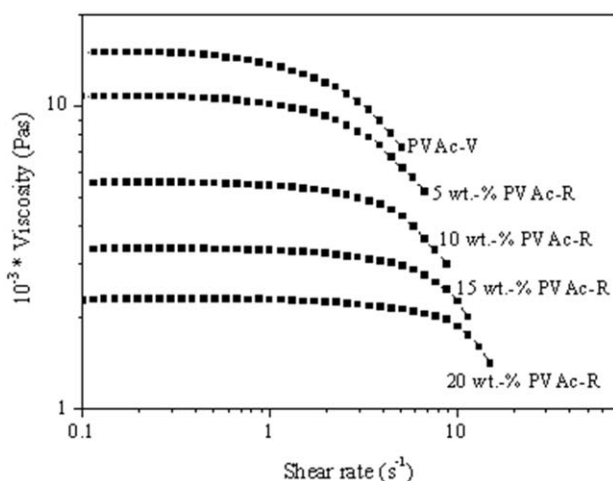


Figure 7. Log η vs. log $\dot{\gamma}$ curves (at 80°C) of PVAc-V mixed with different concentrations of oligomeric PVAc-R.

For the blends, η_0 decreases with increasing oligomer concentration (Figure 6, squares; Supporting Information Table S2) due to the plasticization effect since the addition of oligomeric PVAc-R causes a weakening of the intermolecular interactions in PVAc-V leading to a lower flow resistance. The zero-shear viscosities of the PVAc blends follow an exponential reduction with increasing plasticizer content (Figure 6, dashed line) similar to observations for plasticized poly(lactic acid) denoted as typical plasticizer concentration effect²⁰ and demonstrated by a drastic drop of η_0 of PVAc-V from 15,000 Pas to 5550 Pas for the blend with 10 wt % oligomer.

Additionally, the measurements show that the Newtonian region extends to higher shear rates indicating an increased viscous behavior as the oligomer content in the blend increases (Figure 7) due to the reduction of the interactions in PVAc-V caused by the oligomers facilitating the slipping of the chains past each other. Thus, PVAc-R serves as lubricant for commercial PVAc.

Determination of Volatile Loss. In addition to the extraction by liquids and the migration in solids, evaporation or the so-called “volatile loss” to the air is a common mechanism for explaining the decrease in additives contents from polymeric materials. Due to the lack of a suitable extracting agent for PVAc-R and the high softness of the blended PVAc sheets leading to problems in migration tests, the loss of the oligomeric PVAc from the PVAc sheets were investigated by evaporation using isothermal thermogravimetry at 80°C for 6 h under argon flow (mass loss curves: Supporting Information Figure S10). The starting value of the mass loss was taken after 20 min where a constant isothermal testing temperature was reached for all samples. Under the given conditions, PVAc-V suffers a weight loss of 1.9% (Table II). With increasing oligomer content the weight loss increases up to 5.3% for B15. The FTIR spectra of the volatile components of the materials show only water vapor in the range of 3500 cm^{-1} to 4000 cm^{-1} and 1300 cm^{-1} to 2000 cm^{-1} as evidenced by the vibrational-rotational bands (exemplary shown for PVAc-V and B12.5 in Supporting Information Figure S11). These signals are more pronounced in the spectra of the blends indicating higher moisture contents.

¹H-NMR spectroscopy of PVAc-R shows that the reduced oligomer exhibits DMSO residues (Supporting Figure S12) with the result that PVAc-R as well as samples containing PVAc-R are slightly hygroscopic. Thus, on the one hand, the oligomer has to be dried before further use. On the other hand, the blends absorb higher amounts of water than the PVAc matrix when stored under atmospheric conditions and the moisture content of the blend, which can evaporate during TGA-FTIR experiments, rises with increasing oligomer concentration. This explains the higher mass loss of the blended PVAc samples in comparison to PVAc-V and the increasing Δm value with higher PVAc-R content in the blend. Consequently, the mass loss of the blends observed in the isothermal thermogravimetry is not a result of thermal degradation or evaporation of oligomeric PVAc. PVAc-R is not volatile indicating a good permanence which could be due to its higher molecular weight compared with common monomeric plasticizers leading to lower chain mobility.

Oxygen Permeability. The oxygen permeability coefficient P of the PVAc-V film was found to be 0.33 barrer (1 barrer = $10^{-11} \text{ cm}^3 (\text{O}_2) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ mmHg}^{-1}$) (Table II), which is in good agreement with that in the literature [$P = 0.49$ barrer (30°C)].¹ All obtained values are approx. a ninth of the coefficient of LDPE [$P = 2.93$ barrer (25°C)]¹ indicating the good barrier properties of the presented plasticized PVAc, but do not quite reach the coefficients of poly(vinyl chloride) or poly(vinyl alcohol). Oxygen permeabilities of the plasticized PVAc sheets were slightly lower than that of pure PVAc (Figure 8). Interestingly, the permeability coefficient of the blends is independent of the oligomer content showing a value in the range of 0.30–0.31 barrer. Therefore, adding the oligomeric PVAc, the good oxygen barrier properties of the PVAc matrix were preserved.

Similar trends were observed for other plasticized polymers, e.g., a decrease of the oxygen permeability by mixing chitosan with PEG⁶¹ or PVC with nitrile rubber,²¹ and a constant value of P while adding PEG or glycerol in cellulose based films.⁶² There are several factors influencing the oxygen permeability in plasticized polymer systems such as the physical state or molecular weight of the plasticizer. A potential reason for the lower oxygen permeabilities of the blends in comparison to that of pure PVAc-V in this study could be that the higher spacing between the chains of PVAc-V due to the plasticization facilitates the diffusion of the blend components through the matrix

Table II. O₂ Permeability Coefficient (23°C; 0% Relative Humidity) and Weight Loss Δm Determined by Iso-Thermal TGA (80°C; 6 h) of the Blended PVAc Sheets

Sample	w (PVAc-R) %	P barrer	Δm %
PVAc-V	0	0.33 ± 0.03	1.9
PVAc-B5	5	0.31 ± 0.03	3.5
PVAc-B7.5	7.5	0.30 ± 0.02	3.7
PVAc-B10	10	0.30 ± 0.02	4.2
PVAc-B12.5	12.5	0.31 ± 0.01	5.0
PVAc-B15	15	0.30 ± 0.01	5.3

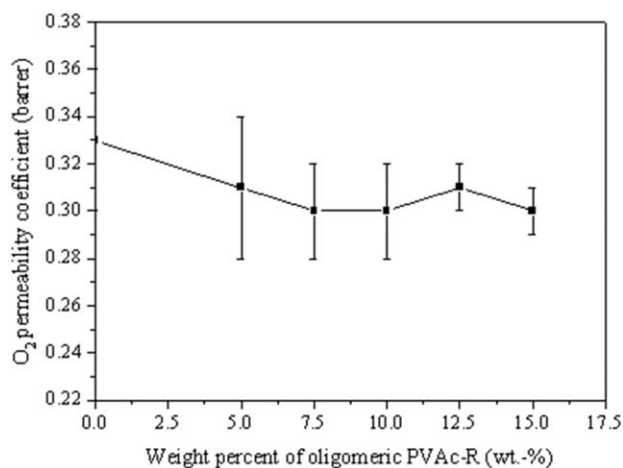


Figure 8. Influence of the concentration of PVAc-R in the blend on the O₂ permeability coefficient of the PVAc matrix.

restricting the oxygen transport. This is in accordance with an explanation reported in the literature.⁶¹

CONCLUSIONS

Telomerization of vinyl acetate using CCl₄ followed by mild reduction with NaBH₄ in DMSO presents an effective method to synthesize thermally stable and oligomeric PVAc with exact $X_n = 10$ in good yields. Reduction of the Cl end groups is mandatory to prevent HCl elimination, which triggers HOAc elimination leading to a low thermal stability and complete decomposition of the material within a few days at ambient temperature.

The reduced oligomeric PVAc proves to be an efficient plasticizer for commercial, brittle PVAc as it exhibits a high miscibility with the PVAc matrix and a good permanence, and improves the processability of the blends. Moreover, the plasticized sheets exhibited ~10% lower oxygen permeability coefficients than the commercial PVAc. Both the plasticizing effect as well as the miscibility of the PVAc components can be explained by a reduction of the inter-molecular interactions of PVAc leading to negative deviations of the T_g values of the blends from Fox' additivity rule. Because of the high flexibility and the good oxygen barrier properties combined with clear advantages in the thermoplastic processability compared with e.g., poly(vinyl chloride) or poly(vinyl alcohol), good the plasticized PVAc in this study presents a promising alternative for barrier materials especially in the field of packaging, e.g., for the replacement of LDPE in multilayer structures.

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