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Effect of side chain length and degree of polymerization on the decomposition and crystallization behaviour of chlorinated poly(vinyl ester) oligomers

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ABSTRACT

Four members of a homologous series of chlorinated poly(vinyl ester) oligomers $CCl_3–(CH_2CH(OCO(CH_2)_mCH_3))_n–Cl$ with degrees of polymerization of 10 and 20 were prepared by telomerisation using carbon tetrachloride. The number of side chain carbon atoms ranges from 2 (poly(vinyl acetate) to 18 (poly(vinyl stearate)). The effect of the *n*-alkyl side chain length and of the degree of polymerization on the thermal stability and crystallization behaviour of the synthesized compounds was investigated.

All oligomers degrade in two major steps by first losing HCl and side chains with subsequent breakdown of the backbone. The members with short side chains, up to poly(vinyl octanoate), are amorphous and show internal plasticization, whereas those with high number of side chain carbon atoms are semi-crystalline due to side-chain crystallization. A better packing for poly(vinyl stearate) is also noticeable. The glass transition and melting temperatures as well as the onset temperature of decomposition are influenced to a larger extent by the side chain length than by the degree of polymerization. Thermal stability is improved if both the size and number of side chains increase, but only a long side chain causes a significant increase of the resistance to degradation. This results in a stabilization of PVAc so that oligomers from poly(vinyl octanoate) on are stable under atmospheric conditions. Thus, the way to design stable, chlorinated PVEs oligomers is to use a long *n*-alkyl side chain.

1. Introduction

Poly(vinyl esters) (PVEs) $(–(CH_2CH(OCO(CH_2)_mCH_3))_n–)$, including poly(vinyl acetate) (PVAc) as the most important member, present an interesting group of polymers due to the dependence of their properties on the side chain length. Just like other polymers carrying n-alkyl side chains [1–4], PVEs with a lower number of side chain carbon atoms are amorphous [5]. Internal plasticization occurs up to a critical number of carbon atoms, where the side chains can crystallize [6,7]. These side chain crystallisable polymers (comb-like polymers) were widely investigated [7–16]. Due to a spacing of about d_{100} = 4.2 Å in the wide-angle region of X-ray diffraction patterns, it was concluded that the side chains can pack hexagonally into paraffin-like crystallites. The crystallization results in an alternating crystalline-amorphous layered structure consisting of amorphous main chain and crystalline side chain domains. Reflections in the small-angle region present the domain spacing of the layered structure. In addition to the crystallization behaviour, the side chain length affects the decomposition of PVEs since a decreasing thermal stability with higher length of the n-acyl portion up to poly(vinyl caproate) was found [17–19]. Moreover, PVAc degrades in an autocatalytic reaction, whereas the pyrolysis of the other poly(vinyl esters) occurs rather by first-order kinetics. Generally, they decompose in two major steps by zip elimination of acids from the side chains [17–19].

In case of oligomeric poly(vinyl esters), the effect of the side chain size on the properties has not been investigated. However, the characteristics mentioned before provides the opportunity to prepare PVEs oligomers with tuneable properties. Oligomers have received great interest due to their low degrees of polymerization (X_n) and have been applied in many areas, especially as additives, e.g. as plasticizers for plastics [20,21], or as compatibilizers for the better compounding of polymers with fillers [22,23]. In addition,

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telomeres, presenting oligomers with very low X_n synthesized by radical polymerization using a chain transfer agent (telogen) in high concentrations (telomerisation) became important owing to their α,ω-difunctionality and were used e.g. as cold flow improvers for fuels [24] or for coatings [25].

Within these fields of application, oligomers are exposed to various influences, e.g. to thermal energy in compounding processes or to atmospheric conditions during storage. As a consequence, degradation occurs resulting in an irreversible deterioration of the properties and a lower performance of the materials. Thermal decomposition presents the breaking of chemical bonds caused by thermal energy in the absence of other degradative influences. For many polymers, the thermal stability is characterized by breaking of the weakest bond, i.e. it is determined by the bond energy [26,27]. Thus, the investigation of the decomposition behaviour, in combination with thermal properties such as the melting temperature, is necessary to ensure a high stability and optimal quality of the oligomers during melt processing and usage. This is especially of interest if they carry labile groups, which can decrease their resistance to degradation and consequently, their applicability. For example, in case of PVAc, it was observed that telomeres synthesized by telomerisation using carbons tetrachloride (CCl_4) or chloroform became colored on standing or were reduced based on the assumption that the chlorinated end groups might not be stable [28–31].

Herein, we present a study on the preparation of a homologous series of chlorinated PVEs oligomers with varying number of carbon atoms from 2 (PVAc) to 18 (poly(vinyl stearate) (PVSt) by telomerisation of vinyl esters (VEs) using CCl_4 as well as on the examination of the impact of the side chain length on their thermal stability and crystallization behaviour. This analysis was performed for degrees of polymerization (X_n) of 10 and 20 in order to compare it with the dependence of the properties on X_n. Concerning the decomposition, the interesting question arises if rather a longer side chain or a higher degree of polymerization stabilizes the instable, oligomeric PVAc (cf. previous section). The poly(vinyl esters) used in this study were PVAc, poly(vinyl octanoate) (PVOc), poly(vinyl myristate) (PVMy) and PVSt.

2. Experimental

2.1. Materials

Vinyl acetate (VAc; 99%; boiling point $K_p = 72\,^\circ C$ (760 mmHg)), vinyl stearate (VSt; melting point $F_p = 35–37\,^\circ C$) and carbon tetrachloride (99,9%) were from Sigma Aldrich, vinyl octanoate (VOc; $K_p = 80\,^\circ C$ (7 mmHg)) and vinyl myristate (VMy; 99%; $K_p = 148\,^\circ C$ (4.8 mmHg)) were obtained from abcr GmbH. Sodium hydroxide (NaOH; ≥97%), sodium sulfate (Na_2SO_4; 99.99%), hydroquinone (>99%) and n-hexane (≥99%) were purchased from Merck, acetone and methanol were from Julia Hoesch and 2,2′-azobisisobutyronitrile (AIBN; >98%) from Fluka Chemicals. VAc was distilled under argon flow before use to remove the inhibitor. VOc and VMy were purified by washing with 10 wt.-% aqueous NaOH and deionised water, and drying over Na_2SO_4. All other chemicals were used as received.

2.2. Determination of chain transfer constants

A 250 mL three-neck round-bottom flask with argon gas inlet, reflux condenser, and mechanical stirrer was loaded with 5 g vinyl ester, 0.05 g (0.31 mmol) AIBN and the concentrations of CCl_4 given in Table 1. The flask was purged at room temperature with argon for 15 min while stirring at 120 rpm. After heating the mixture to 70 °C under argon and stirring, polymerization was interrupted at low conversion by addition of a small amount of hydroquinone and cooling to room temperature. The time required to achieve low conversions was judged by pilot runs. Concerning PVAc, unreacted vinyl acetate and CCl_4 were removed by distillation under reduced pressure. For the purification of PVSt, the mixtures were dissolved in n-hexane and poured into acetone. PVOc and PVMy were purified by pouring into methanol. After that, all polymers were dried under vacuum. Table 1 shows the yields and molecular weights of the products.

2.3. Telomerisation of vinyl esters using CCl_4 as transfer agent

A 250 mL three-neck round-bottom flask with argon gas inlet, reflux condenser, and mechanical stirrer was charged with 10 g vinyl ester, 0.10 g (0.61 mmol) AIBN and the concentrations of CCl_4 given in Table 2. 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. Polymerization was interrupted by cooling the reaction mixture to room temperature. The sample designation used in the following contains the type of the poly(vinyl ester) and the degree of polymerisation, e.g. PVAc-10 stands for poly(vinyl acetate) with $X_n = 10$.

2.4. Purification of the poly(vinyl esters)

2.4.1. Poly(vinyl acetates)

The viscous mixtures were carefully dried under vacuum at room temperature (PVAc-10) or at 35 °C (PVAc-20) to give tacky, slightly yellow colored and viscous oligomers. PVAc-10: Yield: 11.3 g (88%). GPC: $M_n = 1020\,g\,mol^{-1}$, $M_w = 1500\,g\,mol^{-1}$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.71–1.80 (br d, 2H), 1.93–2.00 (t, 3H), 2.15–2.46 (m, 2H), 2.83–3.11 (m, 2H), 4.82 (br s, 1H), 5.32–5.54 (m, 1H), 6.28–6.42 (m, 1H). PVAc-20: Yield: 10.4 g (90%). GPC: $M_n = 1860\,g\,mol^{-1}$, $M_w = 3580\,g\,mol^{-1}$.

2.4.2. Poly(vinyl octanoates)

The slightly viscous reaction mixtures were washed with methanol and then dried under vacuum at 50 °C to give colourless and viscous liquids. PVOc-10: Yield: 7.9 g (52%). GPC: $M_n = 1920\,g\,mol^{-1}$, $M_w = 2630\,g\,mol^{-1}$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.79–0.83 (t, 3H), 1.01–1.33 (s, 8H), 1.43–2.00 (m, 4H), 2.08–2.51 (m, 4H), 2.83–3.11 (m, 2H), 4.80–5.11 (m, 1H), 5.20–5.54 (m, 1H), 6.27–6.44 (m, 1H). PVOc-20: Yield: 9.5 g (76%). GPC: $M_n = 3520\,g\,mol^{-1}$, $M_w = 4370\,g\,mol^{-1}$.

2.4.3. Poly(vinyl myristates)

The viscous mixtures were washed with methanol and then dried under vacuum at 50 °C to give waxy, cloudy and colourless oligomers. PVMy-10: Yield: 6.9 g (54%). GPC: $M_n = 2730\,g\,mol^{-1}$, $M_w = 4220\,g\,mol^{-1}$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.79–0.83 (t, 3H), 0.99–1.36 (m, 20H), 1.43–1.95 (m, 4H), 2.10–2.35 (m, 4H), 2.81–3.11 (m, 2H), 4.79–5.06 (m, 1H), 5.19–5.54 (m, 1H), 6.21–6.44 (m, 1H). PVMy-20: Yield: 9.4 g (82%). GPC: $M_n = 5390\,g\,mol^{-1}$, $M_w = 11{,}780\,g\,mol^{-1}$.

2.4.4. Poly(vinyl stearates)

The solid mixtures were dissolved in 80 mL n-hexane and poured into 400 mL acetone. The precipitates were isolated by decanting off the solvents, and dried under vacuum at 60 °C to give solid, cloudy and colourless products. PVSt-10: Yield: 8.0 g (59%). GPC: $M_n = 3310\,g\,mol^{-1}$, $M_w = 4560\,g\,mol^{-1}$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.79–0.83 (t, 3H), 0.99–1.36 (m, 28H), 1.43–1.99 (m, 4H), 2.10–2.33 (m, 4H), 2.80–3.10 (m, 2H), 4.66–5.06 (m, 1H), 5.22–5.54 (m, 1H), 6.23–6.44 (m, 1H). PVSt-20: Yield: 9.4 g (82%). GPC: $M_n = 6250\,g\,mol^{-1}$, $M_w = 8200\,g\,mol^{-1}$.