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Novel blends of alternating propene-carbon monoxide copolymers and styrenic copolymers

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Summary

Alternating propene-carbon monoxide copolymers (P-CO) were melt-blended with polystyrene, poly(styrene-co-acrylonitrile) (SAN), and with poly(styrene-*co*-maleic anhydride) (SMA). P-CO forms homogeneously miscible blends with SAN containing 25 wt% AN at the investigated blend compositions. The transparent blends have single, intermediate glass transition temperatures that fit the Fox equation. The elastic properties of P-CO at room temperature disappear upon blending with SAN because the T_g is driven above RT. Polystyrene and SMA are not miscible with P-CO and form heterogeneous blends with two glass transitions. This demonstrates that both the polarity of the styrenic copolymer and the nature of the comonomer govern its phase behavior.

Introduction

Alternating copolymers of α-olefins and carbon monoxide form a new class of materials with a wide variety of physical and mechanical properties (1,2). These polyketones can be obtained by polymerization with suitable palladium catalysts. Molecular weight and structure, and thus physical and mechanical properties of the materials can be adjusted by controlled variation of the catalyst, polymerization conditions and the α-olefin (1,2). Alternating copolymers of propene and carbon monoxide (P-CO) of high molecular weight are elastic and transparent at room temperature (T_g = 20-27°C). The stress-strain behavior of P-CO alternating copolymer of sufficiently high molecular weight ($\overline{M}w \geq 100$ kg/mol) resembles that of chemically crosslinked rubbers while retaining melt-processibility (3). Accordingly, these poly(propene-ketone)s may be applied as the rubbery component providing toughness in two-phase blends with glassy polymers (4).

An attempt to improve the impact strength of poly(methyl methacrylate) (PMMA) by solution blending with an amorphous propene-carbon monoxide copolymer (P-CO) has been described (5). This approach was not successful because the P-CO was found to be homogeneously miscible with the PMMA. More importantly, the applied P-CO did not have rubber-like properties, because the molecular weight was only 20 kg/mol (3).

Impact modification of styrenic copolymers like styrene-acrylonitrile (SAN) or styrene-maleic anhydride copolymer (SMA) might be possible by blending with a small amount of P-CO alternating copolymer which exhibits rubber-like behavior at room temperature. If the P-CO can be dispersed as discrete, microscopic domains in the glassy matrix, a rubber-toughening effect may be expected in the heterogeneous, yet transparent blend (4).

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Full miscibility is not very beneficial, since this would cause a lowering of the glass transition temperature of the glassy matrix and loss of the rubbery behavior of the P-CO (4). Partial miscibility might be achieved by tuning the copolymer content of the styrenic copolymer (6-8). In this paper the miscibility behavior of melt-blended mixtures based on alternating propene-CO copolymer with styrenic copolymers of different polarity is presented (9).

Experimental

Materials

Alternating propene-carbon monoxide copolymers were prepared in a 300 mL Roth reactor with $[Ph_2P(CH_2)_3PPh2Pd(NCCH_3)_2](BF_4)_2$ as catalyst precursor, which was prepared by reacting $[Pd(NCCH_3)_4](BF_4)_2]$ (1 mmol) with $Ph_2P(CH_2)_3PPh_2$ (1 mmol) in 50 mL of acetonitrile at room temperature (2b). The product was isolated by filtration and the solvent was removed *in vacuo*. The white solid was characterized by NMR and elemental analysis. Anal. calcd. for $C_{32}H_{34}P_2N_2B_2F_8Pd$ (788.61 g/mol): C, 48.7; H, 4.3; N, 3.6, found: C, 47.8; H, 4.2; N, 3.9. Copolymerizations were typically performed with 0.03 mmol of catalyst and 0.25 mL of MeOH in 150 mL of CH_2Cl_2. Propene was condensed into the intensively stirred catalyst solution for 30 min. at a pressure of 11 bar. Subsequently, a CO-pressure of 50 bar was applied for 48 hrs. At the end of the polymerization, the monomers were vented, catalyst residues removed by filtration over silica gel and colorless films of the P-CO were obtained by slow evaporation of the solvent. Residual traces of CH_2Cl_2 were removed by drying at 35-60°C in a vacuum oven overnight. Table I lists molecular weights and glass transition temperatures of the P-CO copolymers that were applied in this work.

Table I Alternating propene-CO copolymers used in this study

Polymer designation	$\overline{M}n$ (kg/mol)	$\overline{M}w$ (kg/mol)	$\overline{M}w / \overline{M}n$	T_g (°C)
P-CO V 40	213	432	2.6	24
P-CO V 60	87	160	1.8	26
P-CO V 70	53	100	1.9	20-27$^{a)}$

$^{a)}$ Glass transition temperature depends on thermal history of the sample, see Figure 1.

Poly(styrene-*co*-acrylonitrile) (SAN) with an acrylonitrile content of 25 wt% (checked by elemental analysis and ^{1}H-NMR) was used to prepare blends with P-CO V60 and V70 for thermal analysis and tensile testing. SAN samples with 19 and 35 wt% acrylonitrile and poly(styrene-*co*-maleic anhydride) (SMA) with 13.9 wt% maleic anhydride (Arco Chemical Dylark 332) were kindly supplied by BASF AG, Ludwigshafen. SAN 19 and 35 were used for investigating the effect of the AN content of SAN on the miscibility with P-CO. General purpose polystyrene (Styron 686E) and SMA with 28 wt% maleic anhydride were obtained from Dow Chemical Co. Composition, glass transition temperature and molecular weight information on the styrenic copolymers used in this study are given in Table II.

Table II Styrenic copolymers used in this study

Polymer	Designation	$\overline{M_n}$ (kg/mol)	$\overline{M_w}$ (kg/mol)	$\overline{M_w}/\overline{M_n}$	T_g (°C)
Polystyrene	PS	114	237	2.1	102
Poly(styrene-*ran*-acrylonitrile)					
19 wt% AN	SAN 19	83	174	2.1	113
25 wt% AN	SAN 25	98	198	2.0	112
35 wt% AN	SAN 35	68	149	2.2	111
Poly(styrene-*ran*-maleic anhydride)					
14 wt% MA	SMA 14	86	215	2.5	130
28 wt% MA	SMA 28	-	110[a)]	-	163

[a)] Molecular weight information provided by supplier.

Methods

Average molecular weights and polydispersities of the styrenic copolymers were measured by gel permeation chromatography using THF as the eluent. Molecular weight information of the P-CO copolymers was obtained by GPC using chloroform as the eluent. Calibration was done with narrow molecular weight PS standards.

Mixtures of polyketone and styrenic polymers were prepared on a lab-scale, co-rotating twin-screw mini-extruder developed by DSM Research, The Netherlands. The mini-extruder was filled with 3.5-3.8 grams of material in each experiment (max sample load is 4.5 cc). The polyketone was cut into small slices of the desired mass that can easily be given into the extruder. Subsequently, the extruder was loaded with the complementary amount of styrenic copolymer pellets. All blends were mixed for 5 minutes under nitrogen atmosphere at a barrel temperature of 200°C with a screw speed of 100 rpm.

A number of selected blends was injection molded into dumbbell shaped tensile test bars immediately after extrusion. The hot polymer melt was transferred from the mini-extruder to a lab-scale injection molding machine by means of a heated oven with a piston, which at the same time is an integral part of the injection molding machine. The polymer melt is injected into the mould (40°C) by the piston, which is driven by air pressure. The dimensions of the tensile test bars are: overall length 90 mm, thickness 1.5 mm, length and width of central rectangular part 35 and 5 mm, respectively.

Tensile tests were performed at room temperature with a crosshead speed of 10 mm/min on a Zwick 1425 tensile tester equipped with an optical detection system.

Glass transition temperatures were measured by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-7. Heating and cooling rates typically were 20°C/min with samples weighing 5-10 mg. Fourier-transform infrared spectra were recorded at room temperature on a Bruker IFS 113V at a resolution of 2 cm^{-1}. The samples were prepared by casting dilute solutions of extruded blends in dichloromethane onto a KBr plate.

Results and discussion

Thermal behavior of pure P-CO copolymers

The remarkable rubber-like behavior of high molecular weight poly(propene-ketone)s is explained by the formation of ordered segments due to dipolar interactions between the carbonyl groups (3). These interactions appear to be analogous to the interactions that occur in plasticized PVC and it is assumed that crystalline regions in high molecular weight P-CO can act as physical crosslinks (11). The thermal behavior of P-CO V70 as a function of storage time was studied in more detail by DSC. The results are shown in Figure 1. The first heating scan of the solvent evaporated film (A) shows no evidence of crystallinity. The second heating curve, however, was always similar to curve D in Fig. 1. A glass transition at 21°C and a broad exotherm at approximately 55°C were found.

When the DSC sample was stored for 6 weeks at room temperature and analyzed again, a clear melt transition at 50.1°C was found in addition to the T_g at 19.8°C (curve B). The melt transition was even more pronounced after another 5 weeks of storage (curve C). The results show that local ordering develops with time in amorphous P-CO at temperatures close to the T_g. This physical aging process might influence physical properties, performance and lifetime of the copolymer. The melting temperature of the ordered regions depended both on the thermal history of the polymer and on the molecular weight (3). P-CO V70 with $\overline{Mw}$ = 100 kg/mol showed a melt transition at 50-52°C, whereas P-CO V40 ($\overline{Mw}$ = 432 kg/mol) showed a melting peak at 83°C (12).

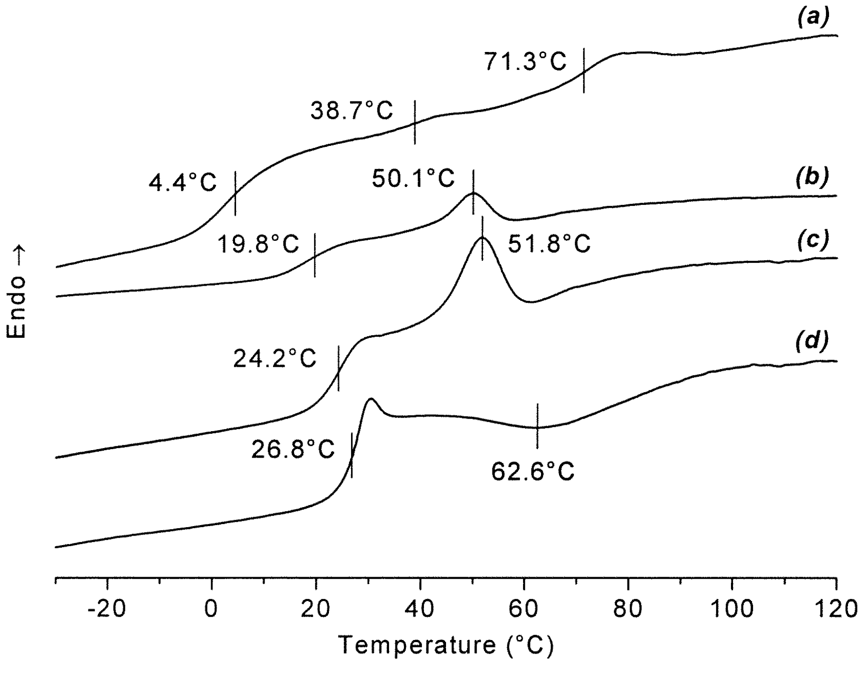

Figure 1 DSC scans of P-CO V70. Presented are the first heating scan of the solvent evaporated film (**A**), the first heating scan of the same sample 6 weeks later (**B**), the first heating scan of the sample after another 5 weeks of storage (**C**), and the second heating scan of the last analysis (**D**).

Miscibility with styrenic copolymers

As mentioned above, blends of alternating P-CO with PMMA were found to be miscible at all compositions (5). Since poly(styrene-co-acrylonitrile) (SAN) is known to be miscible with PMMA and with other polar polymers like poly(styrene-co-maleic anhydride) (SMA), P-CO is expected to be partially miscible with some styrenic copolymers (6-8).

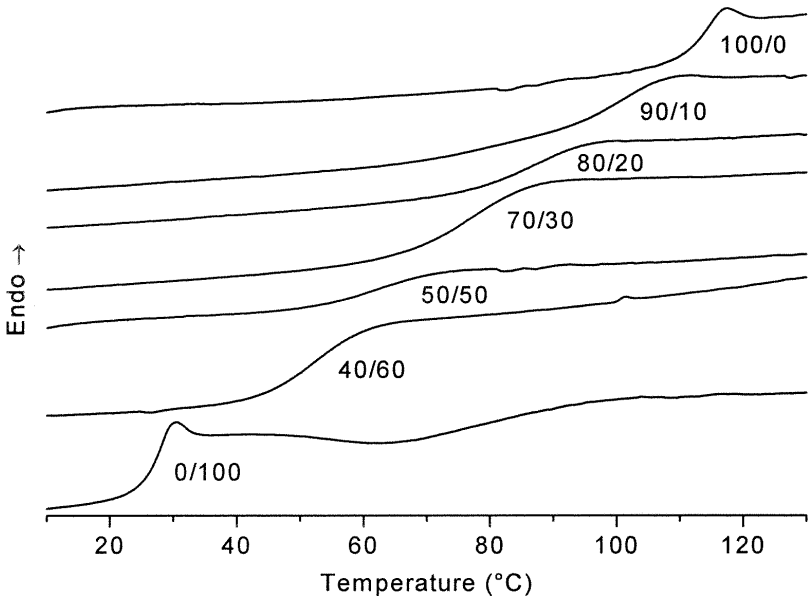

Figure 2 DSC traces of SAN 25/P-CO blends with different blend ratios (100/0 is pure SAN 25). The P-CO was V60 or V70. All curves show second heating scans with a heating rate of 20°/min.

SAN with 25 wt% acrylonitrile was found to be homogeneously miscible with P-CO, as indicated by the optical clarity and the single T_g behavior of the blends at all compositions, as depicted in Figure 2. The glass transitions of the SAN 25/P-CO blends are broader than those of the pure components. The variation of the glass transition temperatures of the blends with the blend ratio is plotted in Figure 3. The dashed line shows the predicted T_g's of the blends according to the Fox equation, as a function of the weight fractions ω and T_g's of the components A and B (10):

$$\frac{1}{T_g} = \frac{\omega_A}{T_{g,A}} + \frac{\omega_B}{T_{g,B}}$$

Single T_g behavior is associated with miscibility of the blend components on the scale of 100 Å, so the P-CO rich phase-separated regions have to be smaller than 100 Å (5).

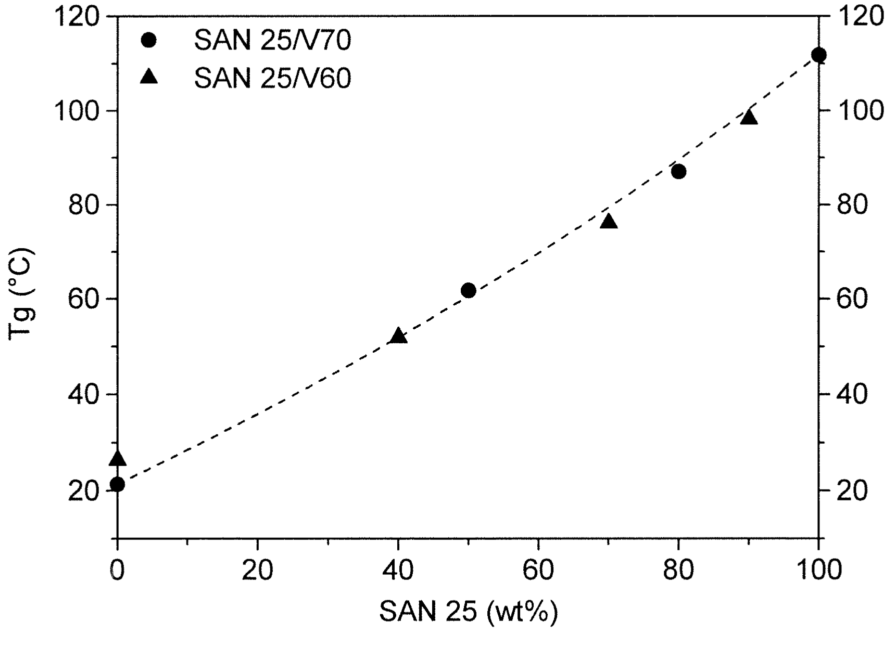

Figure 3 Glass transition temperature (T_g) of SAN 25/P-CO blends plotted against the weight percentage SAN 25. Experimental data were measured by DSC, the dashed line shows the prediction of the Fox equation (10).

Figure 4 summarizes the stress-strain behavior of SAN 25/P-CO blends with up to 60 wt% of the soft phase, i.e. the polyketone. The tensile properties were determined at room temperature, so well below the T_g of the blends (see Fig. 3). The elongation at break (ε_B) of SAN did not increase upon increasing the P-CO content and the modulus (E) remained constant from 0 to 50 wt%, before dropping further at P-CO contents of 40 wt% and lower. These observations contrast with the mechanical behaviour which rubber-toughened thermoplastics typically show: an increasing ductility accompanied by a gradually falling modulus, with increasing rubber content. Materials which contained 20-50 wt% P-CO were stiff and relatively brittle at ambient temperature, but did not start to flow at temperatures above their T_g and became rubber-elastic, which might indicate the presence of microscopic ordered regions in blends with SAN.

It is well known that the miscibility behavior of SMA and SAN, with each other and with other polymers, is strongly affected by the MA and the AN content (6-8). Thus, immiscibility or partial miscibility of P-CO with a styrenic copolymer might be achieved by adjusting the copolymer content of the styrenic copolymer, resulting in a two-phase material. Therefore, blends of P-CO with PS, SAN 19, SAN 35, SMA 14 and SMA 28 were prepared by melt blending. The apolar PS was found to be immiscible with P-CO V 70 (80 wt% PS) as indicated by the presence of two T_g's (31 and 108°C) in the DSC thermogram. Moreover, the PS/P-CO 80/20 blend was weaker and more brittle upon tensile testing than pure PS, which reflects the strong incompatibility between the blend components. The strong incompatibility was also readily seen by the turbid appearance of the blend.

In order to decrease the miscibility with the styrenic copolymers, P-CO V40, with a much higher $\overline{M}w$ than the other P-CO samples, was used for melt-blending with SAN 19 and SAN 35. However, both SAN 19 and SAN 35 form transparent blends (14 wt% P-CO) with P-CO V 40 with a T_g of 93 and 92°C, respectively. The experimental T_g-values at a weight ratio of 80/20 are again in good agreement with the T_g's calculated by the Fox equation (97.1 and 95.6°C), indicating full miscibility. Occurrence of specific interactions between carbonyl groups of the P-CO and nitrile groups of SAN 25 binary blends was investigated by infrared spectroscopy (4,5,8). Changes in the position of the C≡O band (1707 cm^{-1}) or the C≡N band (2237 cm^{-1}) would indicate dipolar interactions that might be responsible for the observed miscibility of P-CO with SAN with 19-35 wt% AN.

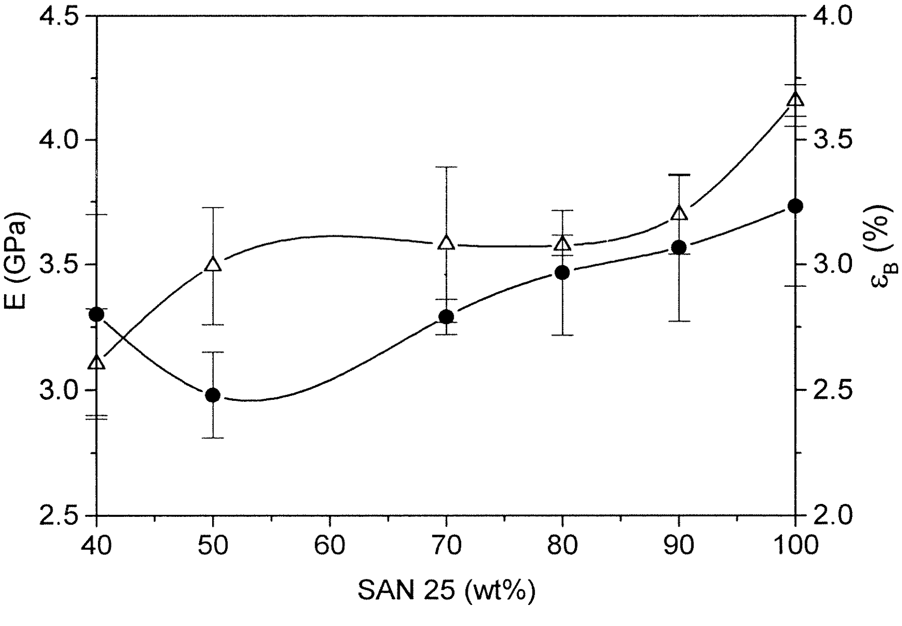

Figure 4 Young's modulus and tensile test elongations to break of SAN 25/P-CO blends as a function of the SAN 25 content at room temperature. Filled circles are elongations at break, open triangles are values of the modulus.

However, blending did not result in detectable shifts (more than 0.5 cm^{-1}) of the bands, as was also seen in PMMA/SAN blends (8). Mixtures of SMA 14 or SMA 28 with 10 - 30 wt.-% of P-CO exhibited gross phase segregation and the phase behavior resembled that of PS/P-CO blends. These results contrast with partial miscibility of SMA 14/SAN 19 blends and complete miscibility of SAN19/SMA 28 blends (6-8).

Conclusions

The phase behavior of blends based on styrenic copolymers and alternating propene-carbon monoxide copolymers was shown to depend on the polarity of the styrenic materials and on the nature of the comonomer. Alternating P-CO copolymer is homogeneously miscible with SAN with 25 wt% acrylonitrile as indicated by the optical clarity and the single T_g behavior of the blends. Blending of P-CO with PS or SMA in a weight ratio of 20/80 resulted in heterogeneous, brittle materials.

The homogeneously miscible SAN/P-CO blends were transparent, brittle materials and did not have the rubber-toughened character that was aimed for. Thus, the P-CO could not be dispersed as microscopic rubber particles in these particular matrix materials, even though the chemical composition of the styrenic copolymer was varied. Nevertheless, it could be of interest for specific applications to improve the flexibility and processability of ABS by lowering the glass transition of the SAN matrix of ABS with P-CO. On the other hand, the modulus of elasticity of pure P-CO copolymer is low (10 - 15 MPa) and can only be increased by introducing crystallinity at the cost of the transparency of the material (1-3). It was demonstrated that this problem can be circumvented by blending amorphous polyketones with suitable other polymers (9). In addition, blending with a low-priced other polymer is usually cheaper than changing the chemical structure of the polyketone.

Acknowledgement

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11. This hypothesis is confirmed by WAXS experiments performed on our P-CO samples: Godovsky, Y.K., Konyukhova, E.V., Chvalun, S.N., Neverov, V.M., Abu-Surrah, A. S. and Rieger B., Macromol. Chem. Phys. submitted
12. There are two possibilities to explain the observed exotherms in the DSC-traces, namely the chemical transition between polyketone and the spiroketale form, (Drent, E.and Budzelaar, H. M., Chem. Rev. 1996, 96, 663 and references therein) or a simple melting. A comparison of our material with the spiroketal form of P-CO demonstrates clearly that these DSC-transitions result from melting.