Synthesis of Polymers with Long Side Chain of N-Alkyl Esters and Their Effects on Pour-Point Depression of Oil

ZENG HUIYANG,* ZHANG WEIBANG, and LI ZHUOMEI

Institute of Polymer Science, Zhongshan University, Guangzhou, People's Republic of China

SYNOPSIS

Three poly(n-alkyl acrylates), PA-14, PA-16, and PA-18, and three poly(vinyl alcohol) aliphatic acid esters, PVA-14, PVA-16, and PVA-18, have been synthesized. They are white crystalline polymers at room temperature and characterized by IR, DSC, SALLS-photometer, and polarizing microscope. Both the melting point and heat of fusion of PVA–esters are larger than those of the corresponding PA–esters, and the sizes of spherulites of PVA–esters are also larger. This may be attributed to the different order of linking in the ester group and the —OH group residue in PVA–esters. In the testing of the effects on pour-point depression of some petrolic oils, only PA-14 and PVA-14 are effective for 0# diesel oil. The influences of molecular weight and molecular weight distribution of PA–esters and PVA–esters upon the pour-point depression of oil are negligible. These results show that the length of n-alkyl side chain of the polyesters plays the most important role in depressing the pour-point of petrolic oil and that the order of linking in the esters group seems to be in no relation to this effect.

INTRODUCTION

Although poly(n-alkyl acrylates) (PA–esters) with long side chains have been used early as a depressant for the pour-point of petrolic oil,[1,2] no studies have been reported on the poly(vinyl alcohol) aliphatic acid esters (PVA–esters) in this application. We suppose that there would exist such a possibility as the structures of PA–esters and PVA–esters are very similar to each other except that their forms of ester linking are in reverse order. Therefore, it is valuable to investigate the structural features of PA–esters and PVA–esters and their effects on the pour-point depression of oil, not only for scientific interest, but also for practical use.

EXPERIMENTAL

Three monomers C_{14}–acrylate (A-14), C_{16}–acrylate (A-16), and C_{18}–acrylate (A-18) were prepared by alcoholysis of methyl acrylate with tetradecanol, hexadecanol, and octadecanol and identified by IR using a 5DX-FTIR spectrometer and by elementary analysis using a Perkin-Elmer 240-C apparatus. They were polymerized in benzene at 60–70°C for 12 h under nitrogen atmosphere with BPO as initiator. The resultant solution after reaction was poured into a large amount of methanol to separate the corresponding polymers PA-14, PA-16, and PA-18 as transparent colorless viscous fluids. After the supernatant was decanted, the viscous fluid was redissolved in benzene (approximately 20% by weight) and the polymer precipitated out as a white solid by pouring the benzene solution into a large amount of methanol. Further purification could be accomplished by washing the solid with methanol several times, which was then dried in vacuum at 50°C to constant weight.

Three poly(vinyl alcohol) aliphatic acid esters, PVA-14, PVA-16, and PVA-18, were synthesized in DMF at 60–70°C by the reaction of poly(vinyl alcohol) (PVA; degree of polymerization = 500) with excess acid chloride for 1–2 h. After reaction, the resultant turbid solution was added into a large amount of water to separate the PVA-esters out as

Table I   Estimation of Residue—OH Groups

Sample	D.E. (%)	D.E. (%, Expt Result)
PVA	88[a]	87.4
PA-14	0	0.45

[a] Commodity specification.

Table II   Values of dn/dc for PA-14 and PVA-14 Samples

Sample	Solvent	n_D^{25}	dn/dc
PA-14	Heptane	1.3857	0.09180
PVA-14	Dioxane	1.4185	0.02315

white solid at room temperature. The product was purified by reprecipitation twice with dioxane as solvent and water as precipitant and finally washed with water to neutrality and then dried in vacuum at 50°C to constant weight.

The degree of esterification (D.E.) was determined by the acetylation method[3] with acetic anhydride anhydrous pyridine solution ($\frac{1}{9}$ by volume) as the acetylation agent. The excess acetic anhydride was analyzed by titration with 1N NaOH. To check the accuracy of the acetylation technique, the estimation of the residue —OH group has been done for two different known samples, as shown in Table I. It is precise to about ±0.5%.

The fractionation of both kinds of polyesters was carried out by the ordinary fractional precipitation method at 30 ± 0.05°C, using 1% benzene solution with methanol as nonsolvent.

The molecular weight of the polymer was determined by Chromatix KMX-6 and *dn/dc* by Chromatix KMX-16 at 25°C with heptane as solvent for PA-14 and dioxane for PVA-14. The values of *dn/dc* are shown in Table II.

The structural features of both kinds of polyesters were examined by 5DX-FTIR IR spectrophotometer, by a Perkin-Elmer DSC apparatus, and by a Ying-Kou LS-1 small-angle laser light-scattering photometer (SALLS) or by a Jiang-Nan XPT-6 polarizing microscope (PLM). The pour-point of oil was determined with a Tian-Jin NGB2 oil freezing point tester.

RESULTS AND DISCUSSION

Identification of Acrylate Monomers and Characterization of PA–Esters

The physical properties and the results of elementary analysis for the acrylate monomers are shown in Table III.

The IR spectra of all acrylate monomers are nearly identical (for example, A-16 as shown by curve 1 in Fig. 1). A strong absorption band appears at 1730 cm^{-1} due to C=O stretching vibration in the ester group and at 1630 cm^{-1} due to C=C stretching vibration, but no absorption at 3400 cm^{-1} due to O—H stretching vibration, indicting that the monomer is a pure α, β-unsaturated ester that does not contain any *n*-alkyl alcohol residues.

IR spectrum for PA-16 is shown in Figure 1 by curve 2. In comparison with curve 1, it can be seen that the absorption band at 1630 cm^{-1} due to C=C

Table III   Physical Properties and Results of Elementary Analysis for Acrylate Monomers

Monomer	bp (°C/3 mmHg) Expt	bp (°C/3 mmHg) Cald[a]	n_D^{25} Expt	n_D^{25} Cald	Elementary Analysis C	Elementary Analysis H	Elementary Analysis O
A-14	151	156	1.4466	1.4470	75.89 (76.06)[b]	12.30 (12.01)	11.82 (11.93)
A-16	175	182	1.4490	1.4495	76.76 (76.97)	12.65 (12.24)	10.59 (10.79)
A-18[c]					77.48 (77.72)	12.90 (12.42)	9.62 (9.86)

[a] Calculated according to literature.[4]
[b] Figures in parentheses are calculated values.
[c] A-18 is gelatinous at room temperature whose bp and n_D^{25} have not been determined.
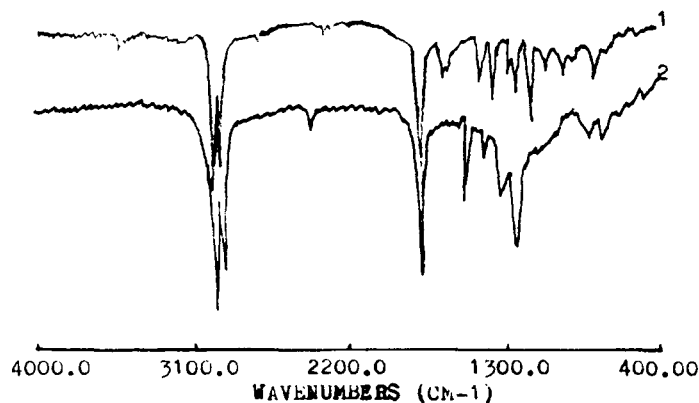
Figure 1 IR spectra for (1) A-16 and (2) PA-16.

does not appear in curve 2. This fact indicates that PA-16 has not been contaminated by the monomer A-16 residue, nor have the other two esters, PA-14 and PA-18.

DSC thermograms have rather sharp endothermic peaks, showing that the PA–esters are crystalline polymers. Their melting points and heats of fusion are listed in Table IV.

Characterization of PVA–esters

IR spectral patterns of PVA–esters are quite similar to those of PA–esters, except that the intensity of absorption at 3300 cm^{-1} due to the stretching vibration of the —OH group would increase as the degree of esterification decreases (for example, PVA-16 as shown in Fig. 2).

The dissolution behavior of PVA–esters greatly depends on the degree of esterification, as shown in Table V. For instance, PVA-16(1) containing —OH up to 40% cannot dissolve in either polar or nonpolar solvent and the other ones with higher D.E. can dissolve in solvents of low dielectric constant

(or low polar solvents). But the dissolution behavior is poor in solvents of very low dielectric constant (e.g., benzene and heptane) due to the presence of —OH, even in a small amount as for PVA-16(4), whereas PA–esters can easily dissolve in benzene and heptane. Evidently, all these facts are related closely to the solvation of alkyl groups and —OH groups and to the aggregation structure of the PVA–ester as well, which will be discussed later.

DSC thermograms with sharp endothermic peaks also show that PVA–esters are crystalline polymers with melting points and heats of fusion higher for those of longer side alkyl chain, the same as with PA–esters (see Table VI). But the sizes of the spherulites of PVA–esters are large enough to be observed very clearly by polarizing microscope, whereas those of PA–ester cannot, as shown in Figure 3.

The fact that PVA–ester can crystallize better than can PA–ester may be attributed to two factors: (1) Since the C — O bond can rotate more freely than can the C — C bond, the steric hindrance effect of the ester side group depends to certain extent on the location of the "free" C — O bond. In PVA–esters, the whole ester side group (including the

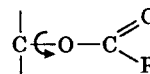**Table IV   Melting Points, Heats of Fusion, and Radii of Spherulites for PA–esters**

Sample	mp (°C)	ΔH_f (cal g^{-1})	R (μm)[a]
PA-14	29	12.1	2.55
PA-16	41	20.1	3.05
PA-18	49	24.0	3.52

[a] The radii were determined by SALLS photometer.[5]

$$\begin{array}{c} O \\ \parallel \\ -C-O- \end{array}$$
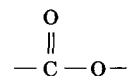
planar structure and chain R) can rotate around the "free" C — O bond attaching directly to the backbone, i.e.,
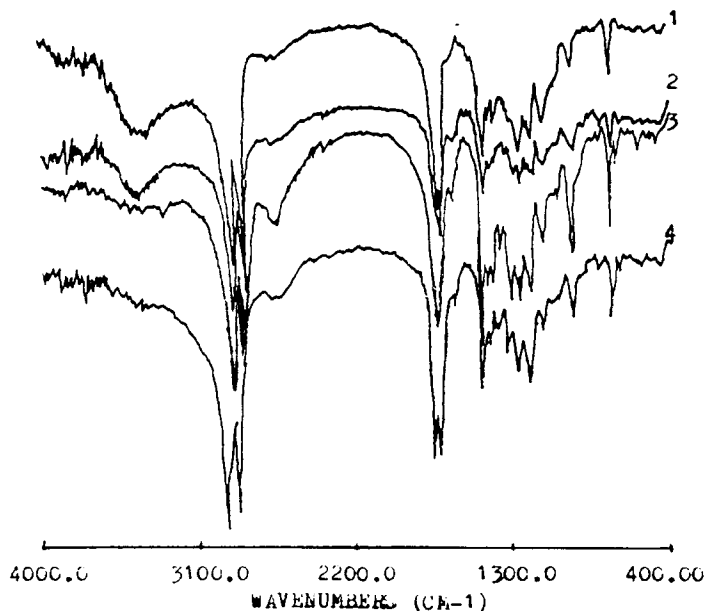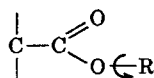
Figure 2 IR spectra of PVA-16. D.E.%: (1) 59.8; (2) 71.1; (3) 87.1; (4) 96.5.

whereas in PA–esters, only the long-chain R can rotate alone around the "free" C—O bond, i.e.,

$$\overset{\mid}{\underset{\mid}{C}}-C\overset{O}{\underset{O-R}{\diagup}}$$

Consequently, in former case, it is easier for the whole ester side group to adjust itself in space to crystallization. (2) The presence of the —OH group in PVA–ester would increase the interaction between macromolecular chains in favor of crystallization. Therefore, PVA–esters can crystallize in larger spherulites, with melting points and heats of fusion higher than those of the corresponding PA–esters, and for the PVA–ester series itself, mp, and

ΔH_f are higher for samples with a greater content of —OH (cf. PVA-16(3) and PVA-16(4) in Table VI).

Depression of Pour-point of Petrolic Oil

All the PA–esters and PVA–esters have been tested for the depression of pour-point of some petrolic oils and are listed in Table VII. The molecular weight and molecular weight distribution of PA-14 and PVA-14 do not show any effect on the pour-point depression (see Table VIII). The influence of amount added on the pour-point depression is shown in Table IX.

Table V Dissolution Behavior of PVA-esters

Sample	D.E. (%)	DMF (36.71)[a]	Ethanol (24.55)	Acetone (20.70)	Butanone (18.51)	1,2-Dichloro Ethane (10.36)	THF (7.85)	Chloroform (4.81)	Benzene (2.28)	Heptane (1.92)
PVA-16(1)	59.8	X[b]	X	X	X	X	✗	X	X	X
PVA-16(2)	71.1	X	X	X	✗	✓	✓	✓	✗	✗
PVA-16(3)	87.1	X	X	X	X	✓	✓	✓	✗	✗
PVA-16(4)	96.5	X	X	X	X	✓	✓	✓	✓	✗

[a] Figures in the parentheses refer to the dielectric constant of the solvent.

[b] ✓ = soluble, ✗ = soluble, but solution slightly turbid, X = insoluble.

**Table VI Degrees of Esterification, Melting Points, and Heats of Fusion for PVA–esters**

Sample	D.E. (%)	mp (°C)	ΔH_f (cal g^{-1})
PVA-14	98.6	50.0	23.8
PVA-16(3)	87.1	65.7	43.7
PVA-16(4)	96.5	58.0	34.7
PVA-18	99.0	67.3	46.2

From these results it can be seen that the effect of pour-point depression is almost the same for PA–esters and PVA–esters. This indicates that the length of the n-alkyl side chain of the polyesters plays an important role in the pour-point depression of petrolic oil, and the order of linking in these ester groups seems to be in no relation to this effect. It is in harmony with the mechanism proposed in our previous work[6] about the pour-point depression behavior of poly(n-alkyl methacrylates). The main point[7] is that the pour-point depressant for the wax-bearing mineral oils cannot prevent the precipitation of the wax crystal, but the depressant adsorbed on the wax surface can reduce the intercrystalline growth to prevent the formation of a three-dimensional wax network. In fact, it has been also observed in our experiment that even in presence of PA-14 or PVA-14 the wax crystalline still precipitates out from the oil at the original pour-point, but with its size much smaller so that the oil can flow fluidly, resulting in a depression of pour-point. It is likely that as soon as the wax crystallines are formed, the alkyl side chains of the polyesters would be adsorbed by the wax solids, leading to cocrystallization, and the polar ester groups would remain outside the wax crystals to prevent their intergrowth or interlocking. Consequently, the length of the n-alkyl side chain suitable for cocrystallization with the wax in the oil is a major influential factor for the pour-point depression, whereas the order of linking in the ester group is merely a minor one.

CONCLUSION

The polyesters PA-14, PA-16, PA-18, PVA-14, PVA-16, and PVA-18 are crystalline polymers at room temperature. The melting points and heats of fusion of PVA–esters are higher than those of the corresponding PA–esters. The sizes of the spherulites of PVA–esters are also larger than that of the corresponding PA–esters. The effect of PVA–esters on the pour-point depression are quite similar to that of PA–esters regardless of the difference in their ester linking. Only PA-14 and PVA-14 are effective for 0# diesel oil. The optimum amount added is 0.10%, and the pour-point depression is 11°C. Their
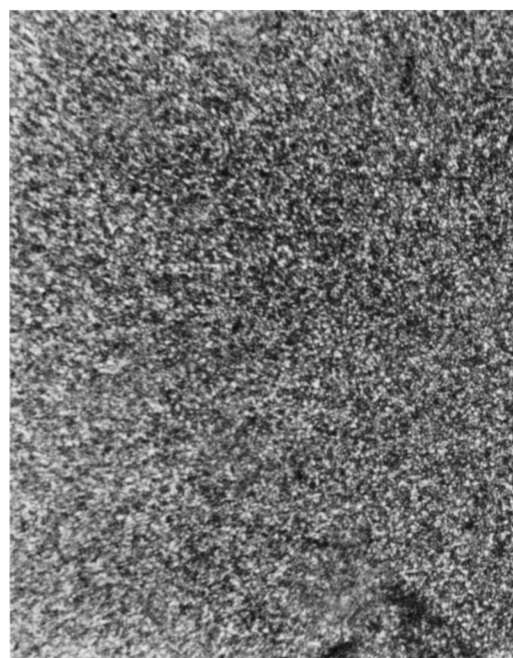
(a)

⊦___100μ___⊣

(b)

⌊__100μ__⌋

Figure 3 PIM patterns for (a) PA–ester and (b) PVA-16 (3).

Table VII   Effect of PA–esters and PVA–esters on the Pour-Point Depression of Petrolic Oil

	0# Diesel Oil		10# Transform Oil		10# Engine Oil	
Sample	Original Pour-point (°C)	Depression Effect (°C)	Original Pour-point (°C)	Depression Effect (°C)	Original Pour-point (°C)	Depression Effect (°C)
PA-14	+2	11	−13	0	−20	0
PA-16	+2	0	−13	0	−20	0
PA-18	+2	0	−13	0	−20	0
PVA-14	+2	11	−13	0	−20	0
PVA-16	+2	0	−13	0	−20	0
PVA-18	+2	0	−13	0	−20	0

Amount of polyester added = 0.1%.

Table VIII   Influence of Molecular Weight and Molecular Weight Distribution on the Pour-point Depression of 0# Diesel Oil

Fraction		1	2	3	4	5	Mixed
PA-14	MW × 10^{-4}	184.1	104.1	35.3	18.6	4.14	
	$-\Delta t$ (°C)	11	11	11	11	11	11
PVA-14	MW × 10^{-4}	235.3	195.6	145.3	69.6	27.9	
	$-\Delta t$ (°C)	11	11	12	12	12	11

Amount of polyester added = 0.1%. $-\Delta t$ is depression effect.

Table IX   Influence of Amount Added on the Pour-point Depression of 0# Diesel Oil

	Amount Added (%)						
	0.01	0.02	0.05	0.07	0.10	0.25	0.50
PA-14 [$-\Delta t$ (°C)]	4		8	10	11	12	11
PVA-14 [$-\Delta t$ (°C)]	2	2	5	8	11	11	10

molecular weight and molecular weight distribution have no relation to this effect.

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