Copolymerization of Ethylene with Vinyl Acetate. II.   Effect of Solvent on Polymer Yield and Molecular Weight*

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Synopsis

In the free-radical solution copolymerization of ethylene and vinyl acetate, polymer yield and molecular weight were found to vary considerably with the solvent used.   Solvents were toluene, benzene, hexane, heptane, and cyclohexane.   Molecular weights were highest in benzene and lowest in toluene and were readily explained by different solvent chain-transfer constants.   Polymer yields were highest in aliphatic solvents and lowest in aromatic solvents including benzene.   This was attributed to different types of interactions of the solvents with radical species.   The saturated aliphatic solvents undergo hydrogen abstraction reactions, but these give reactive alkyl radicals which reinitiate polymer growth.   Toluene also undergoes hydrogen abstraction reactions, but the resultant benzyl radical is resonance stabilized and does not readily reinitiate polymerization. Benzene does not undergo hydrogen abstraction reactions.   The low yields are attributed to complex formation.   A consideration of kinetic theory indicates that complex formation with both initiator and growing polymer radicals is involved.   Differences in viscosity, ethylene solubility, and initiator half-life in the different solvents, as well as induced decomposition of the initiator, were not determining factors.

INTRODUCTION

Solvents can exert a large effect on free-radical polymerization although the mechanism of some interactions is uncertain.   For example, the effect of solvents on rate of polymerization has variously been attributed to complex formation or viscosity effects which alter rate of initiation, propagation, and/or termination.[1-6]   We would like to report on the effect of different solvents on the copolymerization of ethylene and vinyl acetate.

RESULTS AND DISCUSSION

In this investigation, it was found that polymer yield and molecular weight varied considerably with the solvent used.   These results were observed with different initiators under different conditions of synthesis. Representative data are shown in Table I for a series of lauroyl peroxide-initiated polymerizations in hydrocarbon solvents.

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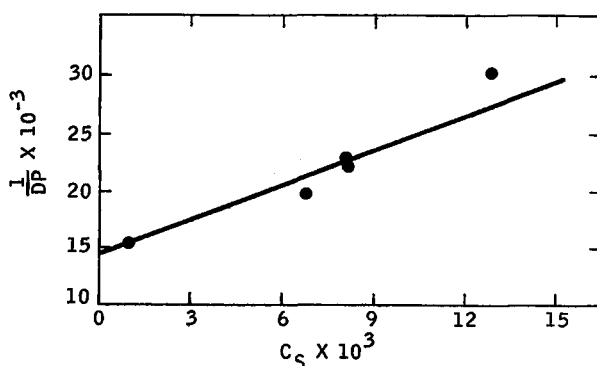
Fig. 1. Chain-transfer constants of solvents vs. copolymer molecular weight.

TABLE I
Effect of Solvent on Lauroyl Peroxide-Initiated Poly(ethylene–Vinyl Acetate)

Solvent[a]	$\bar{M}_n$	Yield, g/mole initiator
Toluene	1190	3600
Benzene	2380	4400
Hexane	1860	6200
Heptane	1610	6400
Cyclohexane	1630	8000

[a] All other conditions identical.

Molecular Weight

The reasons for the large differences in molecular weight with solvent are readily explained by the different chain-transfer constants (C_s) of the solvents.[7]   These data are shown in Figure 1.   The data show a satisfactory inverse relationship between $\bar{M}_n$ and C_s as expected for radical polymerizations.

Yield

The reason for the large variation in yield was not as readily apparent. Changes in solvent can affect yield through chemical or physical effects including ethylene solubility, chain-transfer reactions which result in stabilized radicals, or effect on the initiation process.   These are discussed further.

Ethylene Solubility.   Polymer yield is directly related to monomer concentration, and because the solubility of ethylene is different at the same temperature and pressure in different solvents, this difference could result in variations in yield.   In Table II are shown ethylene solubilities and polymer yields in three solvents.   The data indicate no direct relationship between the two.

TABLE II
Solubility of Ethylene in Solvents Vs. Polymer Yield

Solvent	Solubility of C_2H_4 in Solvent, wt-%[a]	Polymer yield, g/mole initiator[b]
Benzene	20	4400
Cyclohexane	22	8000
Hexane	30	6200

[a] Reference 8.
[b] Lauroyl peroxide.

Solution Viscosity. Solution viscosity can have a large effect on rate of polymerization,[1-5] and viscosities can be different in the different solvents. However, this is not considered to be a factor under the conditions used in the present investigation. Polymer yields (i.e., rates of polymerization) in benzene and cyclohexane were essentially uniform throughout the course of polymerization (Fig. 2). If the viscosity were an important factor, rates would be expected to increase with time.

Initiator Decomposition. In initiator decomposition studies it was found that lauroyl peroxide decomposed faster in benzene ($t_{1/2} = 0.8$ hr) than in cyclohexane ($t_{1/2} = 1.4$ hr). This observation was opposite to the polymer yield relationship and cannot be a determining factor, except for the possibility of induced decomposition of the peroxide. Acyl peroxides are well known to undergo induced decomposition by a variety of reagents and solvents.[9] The effect of induced decomposition (where initiator molecules are consumed in nonpolymerization processes) would be to have a faster rate of catalyst decomposition but a lower polymer yield. This combination was observed in benzene solvent runs compared to cyclohexane and thus suggested the possibility of an induced decomposition of lauroyl peroxide in benzene but not in cyclohexane. This possibility was tested by using azobisisobutyronitrile as initiator because azo initiators are not subject to induced decomposition.[9,10] Data are shown in Table III. It is seen that the same solvent effect on yield was observed with azobisisobutyronitrile as with lauroyl peroxide, which indicates that induced decomposition is not a contributing factor.
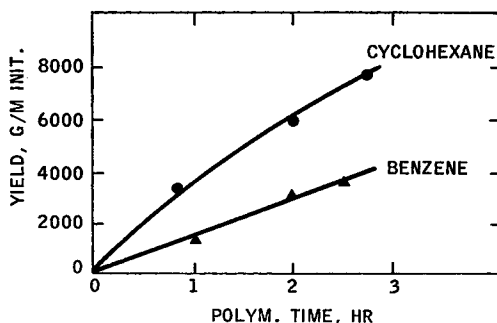

Fig. 2. Profile of copolymer yield vs. polymerization time.

TABLE III
Solvents Effect on Ethylene–Vinyl Acetate Polymerizations Using Lauroyl Peroxide
(L.P.) and Azobisisobutyronitrile (AIBN) as Initiator

	Cyclohexane		Benzene	
	L. P.	AIBN	L. P.	AIBN
Yield of polymer, g/mole initiator	8000	5400	4400	3300

Reaction of Radicals with Solvent

In the present investigation, the reaction of growing polymer radicals with solvent molecules is believed to be the major factor in solvent effects. For many solvents, growing polymer chains can abstract a hydrogen atom from a solvent molecule to give inactive polymer and a free radical derived from solvent. If the solvent radical reinitiates polymerization, no overall decrease in active radicals results, and relatively high yields (but lower molecular weights) are obtained. If, however, the solvent radical is stable and the monomer of relatively low reactivity, it reacts with other active radicals in a termination reaction which effectively removes these from the solution, and low yields result. In both cases interruption of the growing polymer chains reduces molecular weight. These effects are summarized in Figure 3.

The saturated hydrocarbon solvents cyclohexane, hexane, and heptane have relatively high C_s values but give rise to reactive secondary alkyl radicals. These are similar in activity to the primary alkyl radicals of the growing polymer chain (ethylene end) or the initiating undecyl radical obtained from lauroyl peroxide initiator[11] and readily reinitiate polymer growth. The expected result in this case would be low molecular weight and high yield, which was obtained.

Toluene is a good polymerization retarder. It has a high chain-transfer constant C_s, because it undergoes hydrogen abstraction readily with reactive radicals. The resultant benzyl radical is resonance stabilized and should not be very efficient in reinitiating the polymerization of ethylene or vinyl acetate, as both are unreactive monomers. The net result would be low molecular weight and low yield, and this was observed.
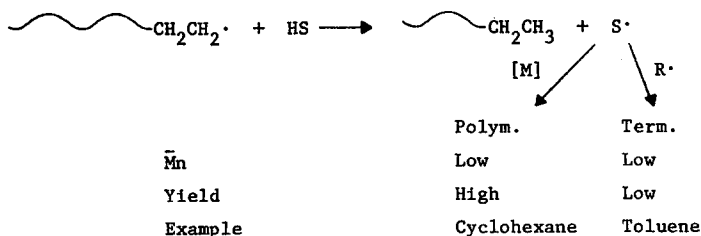

Fig. 3. Effects of chain transfer solvents on copolymer molecular weight and yield.

Benzene, unlike the other solvents, does not readily undergo hydrogen abstraction reactions (low C_s). However, the low yield obtained in benzene indicates some type of interaction with radical species. This interaction may be a complex formation. Although the nature of any complex formed (e.g., π, σ, etc.) cannot be ascertained from these data, a clue as to the radical species involved may be obtained from the yield and molecular weight data. This is shown in Figure 4.

From elementary rate equations[9] (assuming steady state and bimolecular termination), yield, which is proportional to rate of polymerization or R_p, is proportional to $k_p/k_t^{1/2}$ and $\bar{M}_n \propto R_p/R_t \propto k_p/k_t$. If the growing polymer radical complexes with benzene resulting in a species of reduced reactivity (low k_p), the probability of termination would increase (large k_t). The expected result would be low yield ($\propto k_p/k_t^{1/2}$) and even lower molecular weight ($\propto k_p/k_t$). This is not consistent with the data.

If the initiator radicals complex with benzene, reducing the rate of initiation, the expected result would be low yield ($\propto R_t^{1/2}$) but high molecular weight ($\propto 1/R_t^{1/2}$). While this is consistent with the observed data, it is an oversimplification. The initiating undecyl radical produced from lauroyl peroxide has the same structure as the ethylene end of the growing polymer radical, $\sim\!CH_2CH_2$. The solvent would, therefore, be unable to distinguish between these species, and at least some complex formation with both can be expected. In general, therefore, complexation would always give low yields, but molecular weights would depend on the relative amounts of initiator-versus-polymer radical complexation and the amount of cross-termination.

EXPERIMENTAL

Polymerizations were conducted in a stirred autoclave at constant temperature (generally 105°C) and pressure (generally 1100 psig). Initiator

General Effect	Propagating Radical	Initiating Radical
Yield $\propto \dfrac{k_p}{k_t^{1/2}} \cdot R_1^{1/2}$	$\dfrac{k_p}{k_t^{1/2}}$	$R_i^{1/2}$
	(Low)	(Low)
$M_n \propto \dfrac{R_p}{R_t}$	$\dfrac{k_p}{k_t}$	$\dfrac{R_i^{1/2}}{R_i} \propto \dfrac{1}{R_i^{1/2}}$
	(Lower)	(High)

Fig. 4. Effects of complexation of radical species on copolymer yield and molecular weight.

solution was added uniformly during the course of polymerization. A portion of the vinyl acetate was added initially and the remainder was added uniformly during polymerization to maintain a constant composition. Polymerization time was 2.75 hr. Copolymer compositions were approximately 5:1 moles of ethylene:vinyl acetate. Number-average molecular weights were obtained by vapor pressure osmometry. Polymer yields were considered to be total nonvolatile products formed.

The rates of decomposition of lauroyl peroxide in benzene and cyclohexane were determined by infrared spectroscopy by following the disappearance of the acyloxy carbonyl group at ca. 1800 cm^{-1}.[12] The data indicated that the half-lives at 82°C were 0.8 hr in benzene and 1.4 hr in cyclohexane. The result in benzene was in exact agreement with literature values.[13] The half-life in cyclohexane could not be found in the literature.

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