Macromolecules **1983**, *16*, 359-361

although the greater selectivity at higher temperatures would not necessarily be expected.

General. The reactivities of the alkanes in telomerization with tetrafluoroethylene at 125 °C are all nearly the same. The trend of change in the linear alkanes is the same as that observed for photochlorination[21] and for benzoyl peroxide catalyzed chlorination with 2,4,6-trichloro-*N*-chloroacetanilide.[22] The reactivity of the cycloalkanes is less than that expected on the basis of the chlorination results with 2,4,6-trichloro-*N*-chloroacetanilide but about the same as expected from the reactivity with methyl radicals[23,24] and from chlorination with trichloromethanesulfenyl chloride.[25] The comparison of these results is given in Table II.

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(10) The reaction vessel was a Parr Magnedash autoclave of 316 stainless steel.

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Radical Reactions of Highly Polar Molecules. Acetic Acid and Related Compounds as Chain-Transfer Agents in Tetrafluoroethylene Telomerization†

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ABSTRACT: The relative reactivities of the hydrogens in acetic acid and ethyl acetate to abstraction by fluoroalkyl radicals at 125 °C have been determined as follows: $H\text{-}CH_2COOH$, 0.029; $H\text{-}CH_2COOCH_2CH_3$, 0.019; $H\text{-}CH_2CH_2OCOCH_3$, 0.019; $H\text{-}CH(CH_3)OCOCH_3$, 0.10. A separate series of experiments provided less precise reactivities for the abstraction of hydrogen and chlorine from acetonitrile and the chlorinated acetonitriles. The nitrile group stabilizes the intermediate radicals, leading to extensive coupling.

In previous papers we have examined the relative reactivities of halogenated olefins,[1] the chloromethanes,[2] some halofluorocarbons,[3] and several alkanes[4] with tetrafluoroethylene. We now extend the study to a group of compounds related to acetic acid.

The chain-transfer constant for acetic acid is 0.029 and for ethyl acetate 0.039 as calculated by the method of Walling.[5] The relative reactivities of the various hydrogens are as follows: $H\text{-}CH_2COOH$, 0.029; $H\text{-}CH_2COOCH_2CH_3$, 0.019; $H\text{-}CH_2CH_2OCOCH_3$, 0.019; $H\text{-}CH(CH_3)OCOCH_3$, 0.10.

The determination of reactivity followed a method previously reported for chloromethanes,[2] using tetrafluoroethylene as taxogen so that the abstraction is essentially all by fluoroalkyl radicals. The protons in the products from ethyl acetate telomerization were determined by proton NMR, with assignments of peaks as follows (chemical shift values indicated are δ relative to $(CH_3)_4Si$):

$$\underset{5.8}{H}\text{—}(CF_2CF_2)_n\text{—}\underset{3.55}{CH_2}\text{—}COO\text{—}\underset{4.05}{CH_2}\text{—}\underset{1.2}{CH_3}$$

$$\underset{1.95}{CH_3}\text{—}COO\text{—}\underset{5.4}{CH}(\underset{1.4}{CH_3})\text{—}(CF_2CF_2)_n\text{—}\underset{5.8}{H}$$

$$\underset{1.95}{CH_3}\text{—}COO\text{—}\underset{4.8}{CH_2}\text{—}\underset{2.75}{CH_2}\text{—}(CF_2CF_2)_n\text{—}\underset{5.8}{H}$$

The areas of the peaks in the NMR spectra provided a measure of the amounts of each product. The relative reactivities per proton are then estimated by the distribution[6]

$$(3C_\alpha + 2C_1 + 3C_2)/8 = C = 0.039$$

$$C_\alpha = C_2 = {}^3\!/_{16}C_1 \text{ (from NMR area)}$$

where $C = 0.039$ = average chain-transfer constant observed, $C_\alpha = 0.019$ = constant for $H\text{-}CH_2COOCH_2CH_3$, $C_1 = 0.10$ = constant for $H\text{-}CH(CH_3)OCOCH_3$, and $C_2 =$

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† Work done at Union Carbide Corp.

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Table I
NMR[a] Analyses of Telomers
Tetrafluoroethylene with Acetonitriles

products and chem shifts	rel amt, mol %	
CH_3CN		
$H(CF_2CF_2)_nCH_2CN$ 6.0 3.6	43	
$CNCH_2CH_2CN$ 2.6	35	
$H(CF_2CF_2)_nCH(CN)CH_2CN$ 6.0 5.1 2.9	22	
CH_2ClCN		
$H(CF_2CF_2)_nCHClCN$ 6.0 5.5	62.5	75
$Cl(CF_2CF_2)_nCH_2CN$ 3.6	12.5	
$CNCH_2CH_2CN$ 2.6	1.6	25
CNCHClCH$_2$CN 5.0 2.9	3.1	
CNCHClCHClCN 5.0	20.3	
$CHCl_2CN$		
$H(CF_2CF_2)_nCCl_2CN$ 6.0	64	77
$Cl(CF_2CF_2)_nCHClCN$ 5.4	13	
CNCHClCHClCN 5.0	3	23
CNCHClCCl$_2$CN 5.0		
$CNCCl_2CCl_2CN$	20[b]	
CCl_3CN		
$Cl(CF_2CF_2)_nCCl_2CN$	80	
$CNCCl_2CCl_2CN$	20[b]	

[a] The NMR spectra were determined with a Varian HA-100 NMR spectrometer. The reported values are δ relative to tetramethylsilane. [b] The amount of tetrachlorosuccinonitrile was estimated from infrared scans.[10]

Table II

	rel to Cl-CHClCN = 1.0		rel to Cl-CHCl$_2$ = 1.0
H-CH$_2$CN	1.4	H-CH$_2$Cl	1.4
H-CHClCN	2.6	H-CHCl$_2$	2.3
H-CCl$_2$CN	4.9	H-CCl$_3$	4.0
Cl-CH$_2$CN	0.51	Cl-CH$_2$Cl	0.72
Cl-CHClCN	1.0	Cl-CHCl$_2$	1.0
Cl-CCl$_2$CN	1.6	Cl-CCl$_3$	1.9

0.019 = constant for H-$CH_2CH_2OCOCH_3$.

The telomerization of acetic acid with tetrafluoroethylene has been described before but not the reactivity.[7] Telomerization with ethyl acetate has not been described, but several other esters have been reacted with tetrafluoroethylene.[7,8] Cadogen, Hey, and Sharp[9] studied telomerization reactions of styrene with ethyl acetate and other esters and discussed the probability of chain transfer occurring at both the acetyl hydrogens and those α to the oxygen in the ethyl groups. There was no product identification and their argument centered on the comparison of reactivity of ethyl acetate with methyl acetate and diethyl malonate.[10]

The relative reactivities of abstraction in telomerization with one olefin should not be used as a direct prediction of reactivity of a compound with another olefin.

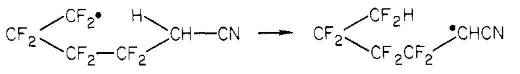
The reactivities of acetonitrile and the three chlorinated acetonitriles were studied by the same method used in the studies with acetic acid and ethyl acetate. Significant coupling of radicals occurred, but by comparisons some relative reactivities (pseudo-chain-transfer constants) have been assigned.

These assignments are to be taken as relative to one another and are not to be compared directly with the values reported for acetic acid and ethyl acetate. The reason for this is that the products are mixtures of telomeric compounds with compounds resulting from coupling. The extent of coupling was determined primarily by proton NMR (Table I), with $CNCCl_2CCl_2CN$ estimated by its infrared spectrum.[11]

The cyano-containing compounds provided relatively low yields of telomer and significant coupling products. The results make it difficult to define and separate the abstraction by fluoroalkyl radicals from that by phenyl radicals. In the chlorinated acetonitrile there was, however, significant abstraction of chlorine so that the fluoroalkyl radicals must have played a significant role.[12]

For an approximation of the reactivities of the various atoms in the acetonitriles, we noted that (1) the amount of coupling steadily decreased with decreasing chlorine content and (2) the ratio of hydrogen to chlorine abstraction is the same for the coupled and the telomeric products for both chloro- and dichloroacetonitrile. Then using the chain-transfer constants calculated by the method of Walling[5] and equations similar to those described above for ethyl acetate, we calculated relative reactivities. For comparison the relative reactivities of chloromethanes[1] are given in Table II.

Only in the telomerization of acetonitrile with tetrafluoroethylene was any product identified which could have arisen by cyclic intramolecular abstraction ("backbiting")[13,14] by the fluoroalkyl chain (eq 1). If any product



(1)

Table III
Telomerization of Functional Chemicals with Tetrafluoroethylene[a]

telogen	telogen, mol	C_2F_4, mol	pressure, psig	telomer, g	telomer, mol	chain length *n*	chain-transfer constant[b]
AcOH	1.332	0.200	250	8.00	0.027	2.38	0.0290
EtOAc	0.908	0.200	250	14.00	0.034	3.30	0.0394
CH_3CN	1.940	0.200	210	5.00	0.038	1.92	0.0769
CH_2ClCN	1.060	0.200	126	2.00	0.016	1.50	0.103
$CHCl_2CN$	0.728	0.200	275	4.00	0.021	1.76	0.126
CCl_3CN	0.554	0.200	225	5.00	0.014	2.24	0.0887

[a] All runs were made using 80 g of telogen, 1.6 g of benzoyl peroxide, and 20 g of tetrafluoroethylene in a 300-cm^3 Parr autoclave at 125 °C for 1 h. [b] The chain-transfer constant is calculated as $C = [C_2F_4]/([\text{telogen}] \times n(\text{av}))$. The values for $[C_2F_4]$ were estimated from the pressure using the vapor pressure of the telogen and assuming ideal behavior.

from this type of reaction was present in the other product mixtures it was not detected. It is possible that it is present in other product mixtures, however, since no effort was made to prove its absence.

Malononitrile was treated with tetrafluoroethylene and benzoyl peroxide but the products were coupled radicals with essentially no incorporation of tetrafluoroethylene.

Experimental Section

The procedure used has been described before.[1-4] The results of the experiments are presented in Table III.

Acknowledgment. Thanks are given to C. B. Strow, Jr., for running the NMR spectra.

Registry No. $H{-}CH_2CN$, 75-05-8; $H{-}CHClCN$, 107-14-2; $H{-}CCl_2CN$, 3018-12-0; $Cl{-}CCl_2CN$, 545-06-2; $CNCH_2CH_2CN$, 110-61-2; $CNCHClCH_2CN$, 84332-52-5; $CNCHClCHClCN$, 84304-00-7; $CNCHClCCl_2CN$, 84304-01-8; $CNCCl_2CCl_2CN$, 6613-50-9; tetrafluoroethylene, 116-14-3; acetic acid, 64-19-7; ethyl acetate, 141-78-6.

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Ordered Structure in Block Polymer Solutions. 2. Its Effect on Rheological Behavior[†]

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ABSTRACT: Polystyrene–polybutadiene (SB) diblock polymer in *n*-tetradecane forms an ordered microdomain structure in which spherical microdomains composed of polystyrene (PS) block chains are dispersed in a solution of polybutadiene (PB) block chains in a simple-cubic-like lattice. The superlattice, which is stabilized by the conformational entropy of the PB chains, is shown to be a primary cause of nonlinear and plastic flow behavior of the solution with an apparent yield stress proportional to ϕ_P, the volume fraction of SB in the solution. The superlattice starts to be distorted, resulting in loss of long-range spatial order of the microdomain structures, at temperatures higher than T_d, the lattice disordering temperature. The lattice disordering is shown to cause an increase of the line profile of the small-angle X-ray scattering (SAXS) maximum and also a discontinuous change of the Bragg spacing with temperature. It is also shown that with increasing temperature across T_d, the flow behavior changes from nonlinear and plastic to linear and non-Newtonian behavior, and the apparent yield stress vanishes. Upon further increase of temperature above the critical temperature T_c, the microdomain structure is dissolved into, more or less, a homogeneous solution of PS and PB; i.e., the system undergoes an order-to-disorder transition. This transition causes the change of the flow behavior from non-Newtonian behavior. An effect of adding homopolybutadiene into the solution on the lattice-disordering phenomenon is also discussed.

I. Introduction

In the previous paper[1] of this series we have explored the microdomain structure of polystyrene–polybutadiene (SB) block polymer in a selective solvent of *n*-tetradecane, good for polybutadiene (PB) chains but very poor for polystyrene (PS) chains as a function of concentration and temperatures. In this paper we shall explore some effects of the microdomain structure and its superlattice on the rheological behavior of the solution.

In section III we shall present some results of small-angle X-ray scattering (SAXS), especially the results indicating two thermal transitions, (i) the lower temperature one associated with a thermal destruction of the *superlattice* (i.e., simple-cubic-like spatial arrangement of the spherical microdomains of PS dispersed in the matrix of PB solution) at the *lattice-disordering* temperature T_d (section III-1) and (ii) the higher the temperature one associated with an *order-to-disorder transition*[2] involving dissolution of the microdomain structure to a nearly homogeneous molecular mixture at the critical temperature T_c (section III-2). Some effects of the *lattice disordering* on the temperature dependence of the line profiles of SAXS maximum and that of the Bragg spacing shall be discussed in section III-1 and III-3, respectively.

In section IV we shall describe changes of the rheological behavior of the solutions with temperature, especially at

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[†] Dedicated to Professor Dr. D. J. Meier on the occasion of his 60th birthday.

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