(4) Charged Rods. This case is identical with case 2 in the dilute regime. TFFF is not useful.

(5) Neutral Globular Chains. For collapsed chains, $R \sim N^{1/3}a$ and D_M is given by

$$D_M = kT/6\pi\eta R \sim N^{-1/3}$$

Our analysis of ref 5 is not applicable to this situation. A recent (unpublished) calculation of Mazur shows that for a rigid sphere, D_T is small and independent of R. Then the result (4) remains valid, leading to $s \sim N^{1/3}$. TFFF is thus applicable to globular chains but is less efficient than for swollen coils.

(6) Charged Globular Chains. Assume Z charges per chain. The main effect of the charges is to increase the osmotic pressure, leading to a higher cooperative diffusion coefficient D_M. We may roughly put (in analogy with eq 7)

$$D_{M_{\text{charged}}} \simeq Z D_{M_{\text{neutral}}}$$

The Soret coefficient is then reduced by a factor of the order of the number of charges. This strong decrease of s will lead rapidly to flat concentration profiles and to zero retention. We do have experiments in that case: No retention is observed with many proteins.[10]

Conclusion

For strongly charged macromolecules, the TFFF technique is expected to break down. This result was frequently reported in the literature without explanations. Our explanation is simple: as soon as macromolecules are charged, the electrostatic repulsions increase strongly the osmotic pressure, and a thermal gradient cannot establish a concentration gradient. The TFFF technique can be used only if the charges are screened by adding enough salt.

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Communications to the Editor

Ring-Opening Polymerization of 2,6-Dialkoxy-5-cyano-3,4-dihydro-2*H*-pyrans:[1] A Novel Monomer-to-Polymer Route to Head-to-Head Alternating Copolymers

Vinyl polymers of head-to-head (H–H) structure have long been the subject of curiosity and have caused recent interest.[2] Long sought after, however, have been synthetic routes that lead to unequivocal and pure H–H structures. Reactions on the polymers are often useful, but clean quantitative conversions are always difficult.[3] Certain, 1,2-disubstituted cyclobutanes, which are accessible by [2 + 2] H–H cycloaddition reactions, would give H–H alternating copolymers upon ring-opening polymerizations. Stille and Chung[4] have prepared several 1,2-disubstituted cyclobutanes and attempted their ring-opening polymerizations. However, all the substituted cyclobutanes failed to polymerize.

In the course of our study of the ring-opening polymerizations of substituted small carbocyclic compounds,[5] we have prepared a series of substituted cyclobutanes and attempted their polymerizations. Most of the substituted cyclobutanes were reluctant to polymerize, confirming the results reported previously.[4] However, we found that the particular adducts between ethyl α-cyanoacrylate and alkyl vinyl ethers were not only found readily but also polymerized well by anionic or cationic catalysts. Interestingly, these adducts were not cyclobutanes but 2,6-dialkoxy-5-cyano-3,4-dihydro-2*H*-pyrans[6] (**1** and **2**), as reported recently by Hall and co-workers.[7] These substituted dihydro-2*H*-pyrans possess the structural moiety in such a way that they are vulnerable to attack by nucleophiles as well as electrophile, resulting in the generation of stable propagating anions and cations for the polymerizations. Thus we have found a new class of unsaturated cyclic ethers that undergo facile ring-opening polymerization. Furthermore, the striking feature of this particular polymerization is that it provides an unprecedented, unique monomer-to-polymer route for H–H alternating copolymer systems. We now report the results of the initial phase of the work.

Dihydro-2*H*-pyrans **1** (mp 16 °C) and **2** (liquid) were prepared according to a procedure[6] similar to that reported already,[7] and they were polymerized[8] with NaCN in Me_2SO at room temperature or with BF_3 in $CHCl_3$ at −30 °C (Scheme I). The results are summarized in Table I. For purposes of comparison, the samples of head-to-tail (H–T) alternating copolymers (**5** and **6**) were prepared by radical copolymerization[9] of ethyl α-cyanoacrylate with alkyl vinyl ethers in benzene with AIBN at 60 °C. Copolymers **3** and **4** were soluble in common solvents such as $CHCl_3$, Me_2CO, and MeC_6H_5 as were copolymers **5** and **6**. The chemical structures of these copolymers were confirmed by their ^1H NMR and IR spectra. However, those spectra exhibited only minor differences, failing to differentiate H–H from H–T microstructures.

The conclusive spectral evidence identifying H–H microstructures of **1** and **2** was secured from their ^{13}C NMR spectra. ^{13}C NMR spectra of **3** and **5** are shown in Figure 1. The most notable structural characteristic of the H–H

Table I
Polymerization[a] of 1 and 2 under Different Conditions

monomer	solvent	monomer/ solvent, g/mL	initiator concn, mol %	temp, °C	time, h	% yield	η_{inh},[b] dL/g
1	$CHCl_3$	0.20	BF_3, 0.5	−30	20	95	0.37
1	CH_2Cl_2	0.10	BF_3, 0.7	−78	20	92	0.37
2	$CHCl_3$	0.18	BF_3, 0.7	−30	22	91	0.27
2	CH_2Cl_2	0.16	BF_3, 0.7	−78	24	88	0.35
1	Me_2SO	0.55	NaCN, 1.5	25	96	89	0.19
2	Me_2SO	0.40	NaCN, 1.9	25	144	60	0.15

[a] The copolymer compositions were estimated to be 1:1 by ^{1}H NMR spectra. [b] Concentration of 0.5 g/dL in $CHCl_3$ at 20 °C.

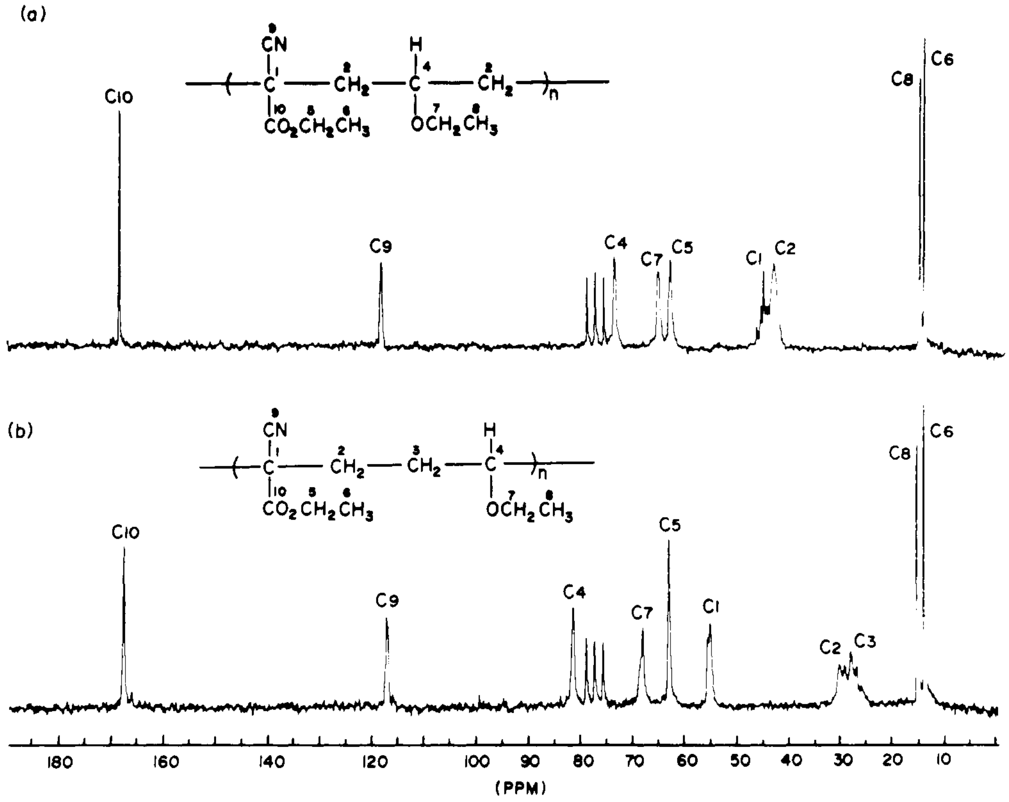

Figure 1. ^{13}C NMR spectra of 3 (b) and 5 (a) in $CDCl_3$ at room temperature. Chemical shifts are referenced to $CDCl_3$ (δ 77.0).

Scheme I

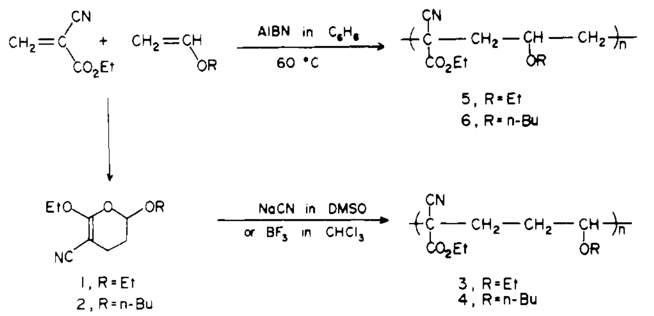

Table II
Thermal Properties of H-H and H-T Copolymers

copoly- mer	type	T_g,[a] °C	degradation temp,[b] °C	
			initial	half-loss
3	H-H	58	324	385
5	H-T	47	347	417
4	H-H	39	275	357
6	H-T	30	317	412

[a] Determined from DSC curves measured on a 910 differential scanning calorimeter (Du Pont Instrument, 990 thermal analyzer) with a heating rate of 10 °C/min in an N_2 atmosphere. [b] Determined from TGA curves measured on a Perkin-Elmer TGS-1 thermobalance with a heating rate of 10 °C/min in an N_2 atmosphere.

alternating copolymers is the presence of two different backbone methylene groups. In the ^{13}C NMR spectrum of 3 (Figure 1b) an extra signal attributable to C-3 was observed at 27.5 ppm. Further, the signals of C-2 and C-3 are shifted to higher field than that of C-2 of the H–T copolymer 5, while those of C-1 and C-4 are shifted to lower field compared with those of C-1 and C-4 of 5. These shifts are those expected based on the chemical shifts[10] estimated for those signals.

Considering the crowded nature of H–H structures, it was of interest to examine the thermal properties of copolymers 3 and 4 in comparison with those of H–T copolymers 5 and 6. Glass transition temperatures (T_g) of copolymers 3–6 and the results of thermogravimetric analyses are shown in Table II. The H–H copolymers exhibited T_g values about 10 °C higher than those of the corresponding H–T copolymers, probably due to chain stiffening by crowded 1,1,2 trisubstitution. This steric repulsion is further reflected by the lower thermal stability of H–H copolymers compared with traditional H–T copolymers.

We are now in the process of applying the present polymerization system to the syntheses of other types of H–H copolymers.

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Registry No. **1**, 83693-33-8; **1** homopolymer, 83693-34-9; **2** homopolymer, 83693-36-1; **3**, 83693-29-2; **4**, 83693-30-5; **5**, 83693-27-0; **6**, 83693-28-1; ethyl α-cyanoacrylate–ethyl vinyl ether copolymer, 83693-31-6; ethyl α-cyanoacrylate–butyl vinyl ether copolymer, 83693-32-7; ethyl α-cyanoacrylate, 7085-85-0; ethyl vinyl ether, 109-92-2.

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(6) The synthesis of **1** exemplifies the procedure. A solution of ethyl α-cyanoacrylate (0.17 mol) in 100 mL of toluene was added slowly to a toluene (150 mL) solution of ethyl vinyl ether (0.2 mol) under N_2. The mixture was allowed to stand at room temperature for 3 days. Solvent and excess ethyl vinyl ether were then removed under reduced pressure. The resulting viscous liquid was placed in a refrigerator (−20 °C) to crystallize. Colorless plate crystals were collected and washed a few times with cold CCl_4: yield 30.8 g (92% yield) of **1**; mp 16 °C; ^1H NMR ($CDCl_3$) δ 5.30 (1 H, t), 3.32–4.40 (4 H, m), 2.15–2.60 (2 H, m), 1.65–1.97 (2 H, m), 1.10–1.45 (6 H, m).

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(8) A representative cationic polymerization procedure was as follows. A solution of **1** (1.97 g) in distilled $CHCl_3$ was introduced into a rubber septum stopper capped glass ampule under dry N_2. The ampule was then placed in a bath maintained at −30 °C and 0.55 mL of $BF_3 \cdot OEt$ was added to the solution. After 20 h the polymerization mixture was poured into a large volume of Et_2O. Precipitated white polymer was collected and reprecipitated from $CHCl_3$ into Et_2O: yield 1.87 g (95% yield) of **3**; η_{inh} = 0.37 dL/g (*c* 0.5 g/dL in $CHCl_3$).

(9) A representative procedure is as follows: In a rubber septum stopper capped glass ampule was placed a solution of ethyl vinyl ether (0.96 g, 12.5 mmol) and 20 mg of AIBN in 10 mL of benzene. The resulting solution was flushed with N_2 for 30 min. The ampule was then placed in a dry ice–acetone bath and the solution was allowed to freeze. To it was added 1.25 g (10 mmol) of ethyl α-cyanoacrylate and the ampule was sealed under vacuum. The ampule was then placed in an oil bath kept at 60 °C. After 10 h the ampule was opened and the viscous solution was poured into a large volume of Et_2O. The precipitated polymer was collected and reprecipitated three times from $CHCl_3$ into Et_2O: yield 0.5 g (30% yield) of **5**; η_{inh} = 0.50 dL/g (*c* 0.5 g/dL in $CHCl_3$). The ^1H NMR spectrum of **5** indicated that the composition of the copolymer was approximately 1:1.

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