tion that $g_N = 1$. It is believed that these are more reliable, at least on a relative basis, than most previously reported values; the higher the molecular weight, the less uncertainty.

Values of the maximum in log J'' are also listed, together with the ratio J_{max}''/J_{eN}^0, which has been observed to be 0.29 for several polymers.[7] According to the theory of Marvin and Oser[5] it should be 0.42, but if this is modified for a most probable distribution of strand lengths the expectation[7] is 0.29. The values of the ratio range from 0.24 to 0.32.

Comparison of M_e values in Table I, and some others calculated simply from J_{max}'' on the assumption that $J_{max}''/J_{eN}^0 = 0.29$, with M_C for those polymers with reported values of the latter[2] gives M_C/M_e ratios in the neighborhood of 2, as recently shown in other compilations.[2,3] However, it can be argued that g_N in eq 3 should be one-half instead of unity.[10,11] In this case, M_C/M_e would be near 4. It is doubtful whether much significance can be attached to this ratio at the present time. For interpreting the magnitudes of viscoelastic properties in the plateau zone, either the entanglement compliance J_{eN}^0 may be used directly or else the spacing M_e recognizing that its absolute value depends on eq 3 with an arbitrary choice of g_N.

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Communications to the Editor

Donor-Acceptor Complexes in Copolymerization. I. Preparation of Styrene-Acrylonitrile Alternating Copolymers in the Presence of Zinc Chloride

The free radical initiated copolymerization of allylic and olefinic compounds with polar monomers, such as acrylonitrile and methyl methacrylate, in the presence of zinc chloride yields copolymers containing concentrations of olefinic monomer higher than normally encountered in the absence of the metal halide.[1,2] The uncatalyzed spontaneous copolymerization of α olefins with these polar monomers in the presence of an ethyl aluminum halide at −78° yields high molecular weight 1:1 alternating copolymers.[3–5]

It has been proposed[6,7] that analogous mechanisms are operative in both cases, *i.e.*, the alternating copolymer results from the spontaneous homopolymerization of an equimolar (olefin–polar monomer $\cdots$ $(C_2H_5)_xAlCl_{3-x}$) complex while the nonequimolar copolymer results from the free radical initiated copolymerization of (olefin–polar monomer $\cdots$ $ZnCl_2$) and (polar monomer–polar monomer $\cdots$ $ZnCl_2$) complexes.

Confirmation of the postulated analogy between the spontaneous formation of equimolar copolymer and the radical-initiated formation of nonequimolar copolymer was demonstrated[7] by the formation of high molecular weight 1:1 copolymer from styrene and methyl methacrylate in the presence as well as in the absence of a free radical initiator. The equimolar copolymer was produced at 25–30° in the presence of $Et_{1.5}AlCl_{1.5}$ alone or together with 2-methylpentanoyl peroxide, irrespective of monomer charge. The presence of the radical catalyst increased the rate of copolymerization and decreased the copolymer molecular weight to a very slight extent, without influencing the 1:1 structure of the copolymer.

Further confirmation of the identity of the spontaneous and catalyzed complex polymerizations has now been obtained in the uncatalyzed as well as radical initiated copolymerization of styrene and acrylonitrile at 60° in the presence of zinc chloride. This system forms a high molecular weight 1:1 alternating copolymer, irrespective of monomer charge.

As shown in Table I, the presence of zinc chloride alone or zinc chloride plus benzoyl peroxide at 60° yields high molecular weight 1:1 copolymers at styrene:acrylonitrile molar ratios of 3:1, 1:1, and 1:3. In the absence of zinc chloride the radical catalyst yields a lower molecular weight copolymer whose composition is dependent on monomer charge. This observation is consistent with conventional radical polymerization.

The formaion of 1:1 copolymer from the styrene–acrylonitrile system but nonequimolar copolymer from other olefin–acrylonitrile systems in the presence of zinc chloride is indicative of the strong electron-donating character of styrene as compared to the other olefins. The S–AN $\cdots$ $ZnCl_2$ complex is either formed preferentially, to the exclusion of the AN–AN $\cdots$ $ZnCl_2$ complex, or the rate of homopolymerization of the former complex is greater than the rate of copolymerization of the two complexes. A similar result has been noted in the attempted spontaneous terpolymerization of cyclopentene, styrene, and sulfur dioxide.[8] Although the cyclopentene–sulfur dioxide and the styrene–sulfur dioxide systems readily copolymerize separately, the termonomer composition gives a copolymer containing only styrene and sulfur dioxide.

The 1:1 copolymer is obtained from a 3:1 styrene:acrylonitrile comonomer charge at 60° even when the

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TABLE I

BULK COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE (AN) IN THE ABSENCE OR PRESENCE OF $ZnCl_2$ AND/OR BENZOYL PEROXIDE (BP) AT 60°

AN in feed, mole %	$ZnCl_2$/AN, mole ratio	BP, mole % (on AN + S)	Time, min	Yield, %	[η], dl/g	N, %	AN in copolymer, mole %
25	0	0.2	30	2.5	0.88	4.67	29.5
50	0	0.2	30	2.1	0.68	6.60	39.5
75	0	0.2	30	5.5	1.30	8.68	49.5
25	0.1	0	40	3.6	2.50	8.72	49.5
50	0.1	0	30	2.8	2.20	8.72	49.5
75	0.1	0	40	6.2	2.08	8.80	50.0
25	0.1	0.2	5	1.8	2.89	8.70	49.5
50	0.1	0.2	5	5.8	1.33	8.71	49.5
75	0.1	0.2	5	5.8	1.60	9.10	50.5

TABLE II

BULK COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE (AN) IN THE ABSENCE OR PRESENCE OF $ZnCl_2$ AND/OR *t*-BUTYL PEROXYPIVALATE (TBPP) AT 25°

AN in feed, mole %	$ZnCl_2$/AN, mole ratio	TBPP, mole % (on AN + S)	Time, min	Yield, %	[η], dl/g	N, %	AN in copolymer, mole %
25	0	1.0	150	2.4	0.82	5.25	32.6
50	0	1.0	150	2.9	1.10	7.10	42.0
75	0	1.0	150	2.9	1.01	9.15	51.5
25	0.1	0	150	0			
50	0.1	0	150	0			
75	0.1	0	150	0			
25	0.1	1.0	35	7.8	5.34	7.98	46.3
50	0.1	1.0	35	10.0	5.13	8.51	48.5
75	0.1	1.0	35	8.1	3.68	8.77	50.0

$ZnCl_2$:AN ratio is increased from 1:10 to 1:2. Similar results have been noted in the styrene–methyl methacrylate–$Et_{1.5}AlCl_{1.5}$ systems.[9]

The influence of temperature on the bulk copolymerization is shown in Table II. Little or no polymer is obtained at 25° after 150 min in the presence of zinc chloride and the absence of a radical catalyst. Thus, the rate of spontaneous homopolymerization of the S–AN · · · $ZnCl_2$ complex is negligible at 25° as compared to 60°.

The radical catalyst, *t*-butyl peroxypivalate, alone in the absence of zinc chloride yields a low molecular weight copolymer whose composition is that of a conventional radical copolymer. Although higher molecular weight copolymer would be expected at 25° than at 60°, the fivefold greater catalyst concentration at 25° is reflected in the similarity of the molecular weights at the two temperatures. However, the presence of zinc chloride and the radical catalyst at 25° yields extremely high molecular weight, essentially 1:1 copolymers, at styrene–acrylonitrile molar ratios of 3:1, 1:1, and 1:3.

The styrene–acrylonitrile · · · $ZnCl_2$ system gives similar results in toluene as in bulk at 60°. However, the use of ethyl acetate as reaction medium inhibits or prevents the polymerization, probably due to complexation with $ZnCl_2$ in competition with acrylonitrile.

The copolymerizations were carried out with distilled monomers in a three-necked round-bottomed flask with magnetic stirring. The zinc chloride was heated for 3 hr at 220° under vacuum before use and mixed with acrylonitrile and styrene at 25 or 60° under a nitrogen atmosphere. The radical catalyst, where used, was then added. The originally homogeneous mixture became heterogeneous as polymerization proceeded due to precipitation of the copolymer. After the desired reaction period, acetone was added to terminate the reaction and dissolve the copolymer. The latter was precipitated by pouring the solution into methanol, filtered, and dried *in vacuo* at 40°.

Copolymer composition was determined by elemental analyses. Intrinsic viscosities were measured in dimethylformamide at 30° in a Ubbelohde viscometer.

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Estimation of Glass Transition Temperatures from Gas Chromatographic Studies on Polymers

In a recent communication, Smidsrød and Guillet[1] showed that thermodynamic data on the interactions between polyisopropyl acrylamide and various gaseous solutes could be obtained by making the polymer the stationary phase in a gas chromatograph. It was also shown that if a solute was used which was a nonsolvent for the polymer, a plot of the logarithm of the specific

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