

The Preparation of Crystalline Polypropylene Sodium Sulfonates and Their Interaction with an Included Sodium Hydroxide Phase

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Synopsis

Sodium sulfonated polypropylenes have been prepared by the slurry chlorosulfonation of polypropylene or propylene-ethylene copolymer followed by hot aqueous sodium hydroxide treatment. Low levels of excess sodium hydroxide were added to the materials to stabilize them against thermal decomposition. It was found that there was a strong interaction between the sodium hydroxide phase and the polymer sodium sulfonate groups which persisted above the nominal melting point of crystalline polypropylene. Evidence for the interaction includes an increased melt viscosity and a greatly increased nucleation rate for the composites as compared to the polypropylene sodium sulfonates not containing the sodium hydroxide phase. The composites have an improved balance of mechanical properties as compared to the materials from which they are prepared.

INTRODUCTION

Ionic bonding in organic polymer systems is of considerable current interest. The linking together of polymer molecules through certain ionic bonds can enhance the mechanical properties of some polymers without seriously detracting from their melt processability.^{1,2} This apparently derives from the reversibility of the ionic bonds under high shear or temperature conditions.

In this study, sodium sulfonate groups were introduced along a polypropylene backbone via light-initiated chlorosulfonation followed by hot aqueous caustic treatment. The chlorosulfonation step results in some chlorination also, and the products were stabilized against thermal dehydrohalogenation by inclusion of low levels of excess sodium hydroxide. It was found that apart from its function as a stabilizer, the sodium hydroxide phase had a profound effect on the properties of the sodium sulfonated polymers. Data are presented on the preparation and properties of these modified polypropylenes with and without an included sodium hydroxide phase.

EXPERIMENTAL

Preparation of Polypropylene Sodium Sulfonates

Chlorosulfonation runs were made in a 5-liter baffled Pyrex reactor with a 22-watt circular fluorescent light fitted exterior to the reactor top. After nitrogen purging to displace the oxygen present, chlorine and sulfur dioxide gases were premixed and added subsurface (total of 18×10^{-3} moles/min) to a stirred slurry of polypropylene in the vehicle. Temperature control was by ice water bath or a West Model JE temperature controller-monitored heating lamp depending on the level desired. In all cases, 200 g of polypropylene powder in 2 liters of vehicle were worked per run. Product powder was washed three times with the vehicle used in the run and dried at $\sim 50^\circ\text{C}$ for ≥ 16 hr in a vacuum oven (~ 10 mm Hg).

The dried chlorosulfonated polypropylene was treated with 3 liters of hot (80°C) aqueous 15 wt-% sodium hydroxide (plus a few drops of Sterox wetting agent) with stirring for 5 hr to convert to the sodium sulfonate form. The powder was water washed five times and dried at $\sim 50^\circ\text{C}$ for ≥ 16 hr in a vacuum oven (~ 10 mm Hg). The dry polymer powder was stabilized with 0.1 wt-% Ionol (added as methanol solution, and methanol was removed under vacuum in a rotating flask) and sodium hydroxide (added in 90/10 methanol/water, and solvent removed as before).

Analyses of Products

Sulfur analyses were by x-ray fluorescence using standards of elemental sulfur in polypropylene. Samples analyzed prior to conversion of the sulfonyl chloride groups to their sodium sulfonate form were cold pressed into tablets for the analysis. Chlorine analyses were done by Galbraith Laboratories.

Crystallinity of polymer powder samples was measured by x-ray diffraction. Alternatively, crystallinity of the molded specimens was estimated by infrared from the ratio of the bands at 995 cm^{-1} to 974 cm^{-1} .³

Polymer Properties

Degree of nucleation of polymer samples was estimated from crystallization half-times using the light depolarization⁴ method or from crystallization temperature⁵ using the Perkin-Elmer DSC-1B at $\Delta T = -10^\circ\text{C}/\text{min}$.

Injection-molded samples for mechanical property evaluation were prepared from the powder on a Frohring Minijector using a barrel temperature of 205°C and a mold temperature of 65°C . Samples were held ≥ 2 days at room temperature prior to testing. Conditions for the various tests are shown in Table I.

In order to eliminate possible orientation effects during injection molding, a number of tests were also run on samples cut from compression-molded plaques. These specimens were aged ≥ 2 days at room temperature prior to testing. Tensile modulus was run according to ASTM D-1530-58T.

TABLE I
Test Procedures for Polymer Evaluation

Test for	ASTM testing procedure	Comment
Flexural modulus	D-790	procedure A
Tensile at yield	D-638 }	Cross-head speed = 2 in./min
% Elongation at yield	D-638 }	
Izod impact	D-256	method C
Melt flow	D-1238L	

The burst strength test is non-ASTM. It involves striking a thermostated 5-mil-thick sheet of material with a pendulum-mounted spherical-shaped impact head and measuring the energy required to rupture and penetrate the sample.

Materials

Polypropylenes were Enjay powders of >93% hot heptane insolubles. They contained no stabilizers.

Impact propylene-ethylene copolymer was a commercial pelletized grade. This material was ground to a fine powder in a Waring Blendor under liquid nitrogen prior to reaction. It contained ~25 wt-% ethylene, had a hot heptane-soluble fraction of ~20 wt-%, and was stabilized. The stabilizers were not removed prior to reaction.

Sulfur dioxide was Matheson anhydrous grade, >99.98% purity, used as received. Chlorine was Matheson high-purity grade, >99.5% purity, used as received.

Carbon tetrachloride, benzene, carbon disulfide, and sodium hydroxide were B&A A.C.S. reagent grades, Code Nos. 1554, 1442, 1552, and 2255, respectively. They were used as received.

RESULTS

Chlorosulfonation of polypropylene gives a product containing both $-\text{SO}_2\text{Cl}$ and $-\text{Cl}$ groups. In order to assess the thermal stability of chlorinated polypropylene containing no sulfonyl chloride groups, a few preliminary chlorination runs were made. Some data on the time required for first bubble (HCl) formation in unstabilized chlorinated polypropylenes as a function of the weight per cent chlorine at 190°C (sample pressed between glass plates) are shown in Figure 1.

Sulfonyl chloride groups on polypropylene are also thermally unstable. In hot-pressing specimens of chlorosulfonated polypropylenes, it was found that >50% of the contained sulfur was lost by a 5-min treatment at 200°C ; hence, XRF measurements for sulfur were made on cold-pressed powder samples.

Data on the effect of vehicle, temperature, and SO_2/Cl_2 ratio in the feed gas on the $\text{SO}_2\text{Cl}/\text{Cl}$ molar ratio in the product are shown in Table II and Figures 2 and 3.

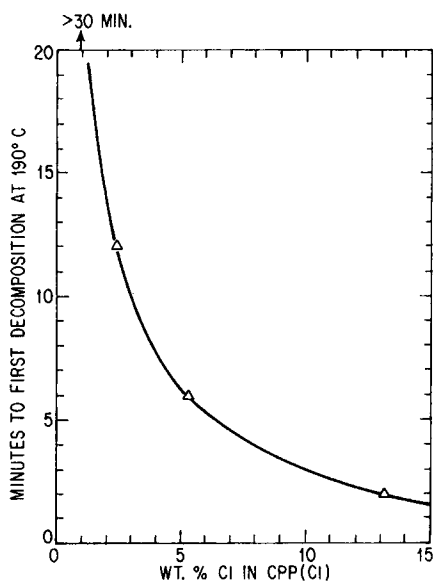


Fig. 1. Thermal stability of chlorinated polypropylene.

Data on the effect of the chlorosulfonation level on the crystallinity of the product are shown in Figure 4. Powder crystallinity data are obtained from x-ray diffraction, and crystallinities of the molded materials are estimated from the appropriate infrared bands after conversion of SO_2Cl groups to SO_3^-Na^+ .

Treatment of chlorosulfonated polypropylene with hot aqueous sodium hydroxide results in essentially complete conversion of the SO_2Cl groups to SO_3^-Na^+ while leaving the chlorine bonded to carbons unaffected, as shown in Table III.

Data on the melt flow properties of the modified polymer, after conversion to their stable metal sulfonate form, are shown in Figure 5. Data are included for the pure polypropylene metal sulfonates and for some of

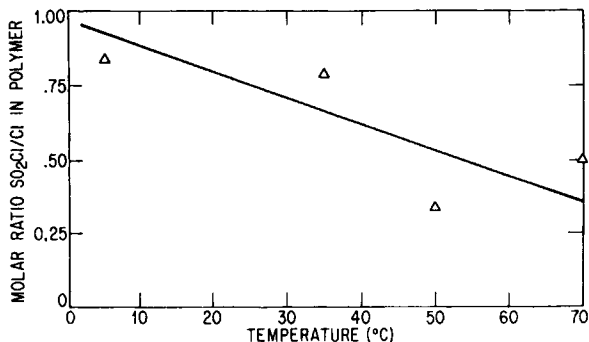


Fig. 2. Ratio of $\text{SO}_2\text{Cl}/\text{Cl}$ vs. temperature in sulfochlorinated polypropylene. Run in CCl_4 ; SO_2/Cl_2 ratio in feed = 2.5.

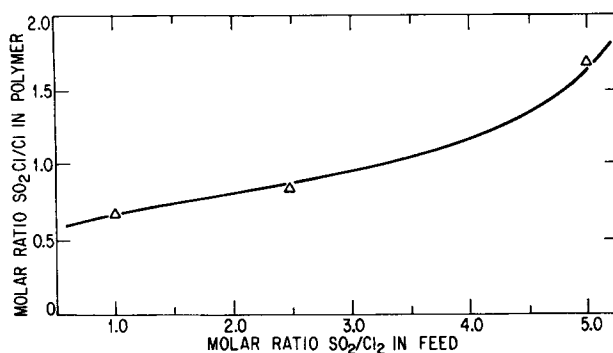


Fig. 3. Ratio of SO₂Cl/Cl vs. feed ratio SO₂/Cl₂ in sulfochlorinated polypropylene. Run in CCl₄ at 5°C.

TABLE II
Data on Slurry Chlorosulfonation of Crystalline Polypropylene

Run no.	Time of reaction, hr	Vehicle	Temp., °C	Feed ratio SO ₂ /Cl ₂ ^a	Product composition, mole-%		Product ratio SO ₂ Cl/Cl
					-SO ₂ Cl	-Cl	
1	2	CCl ₄	5	1.0	3.48	5.10	0.68
2	2	CCl ₄	5	2.5	1.20	1.42	0.84
3	2	CCl ₄	5	5.0	2.77	1.64	1.69
4	2	CCl ₄	35	2.5	2.00	2.54	0.79
5	2	CCl ₄	50	2.5	2.83	8.34	0.34
6	2	CCl ₄	70	2.5	3.82	7.57	0.50
7	2	benzene	35	2.5	1.04	2.53	0.41
8	4	CS ₂	5	5.0	4.77	4.28	1.11

^a Total of 18 × 10⁻³ moles/min feed gas.

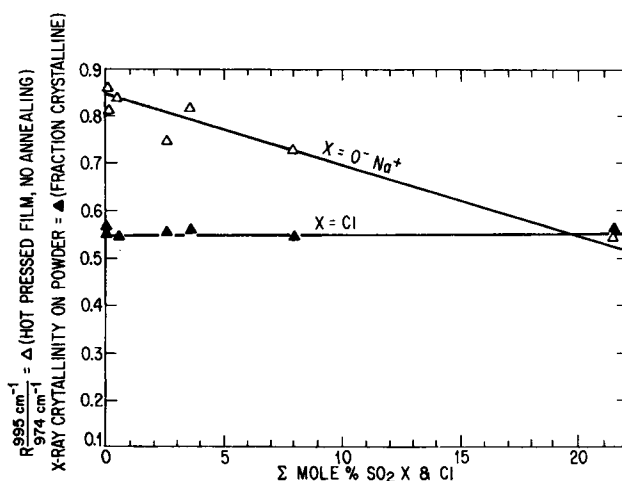


Fig. 4. Effect of level of substitution on polypropylene crystallinity.

TABLE III
Conversion of Chlorosulfonated Polypropylene to Polypropylene Sodium Sulfonates

Sample no.	Chlorosulfonated sample			After aq. NaOH treatment		
	S, wt-% (as SO ₂ Cl)	Cl, wt-% (as C—Cl)	S/Cl	S, wt-% (as SO ₃ ⁻ Na ⁺) ^a	Cl, wt-% (as C—Cl)	S/Cl
1	0.90	1.18	0.76	1.00	1.39	0.72
2	1.82	3.24	0.52	1.87	2.29	0.82
3 ^b	6.44	6.66	0.97	4.29	4.05	1.06

^a By ion exchange with HCl and back titration with standard base.

^b A portion of this sample is rendered water soluble by the hot aqueous caustic treatment; hence, the lower values for both sulfur and chlorine on the nonsoluble portion which was analyzed.

the same resins containing 0.5 wt-% of an included sodium hydroxide phase. Melt indexer shear-stress, shear-rate data at two temperature levels for a polypropylene sodium sulfonate (containing 0.5 wt-% sodium hydroxide) and an unmodified polypropylene of about the same melt flow are shown in Figure 6.

Some representative degree of nucleation measurements, as inferred from the DSC determined crystallization temperature, are shown for selected samples in Table IV. Crystallization half-times and DSC crystallization temperatures are included in Table V.

Mechanical property data on selected samples are given in Tables V and VI for injection- and compression-molded specimens, respectively. The effect of sodium hydroxide concentration on crystallization temperature, modulus, and melt flow of two modified polymers are shown in Figure 7.

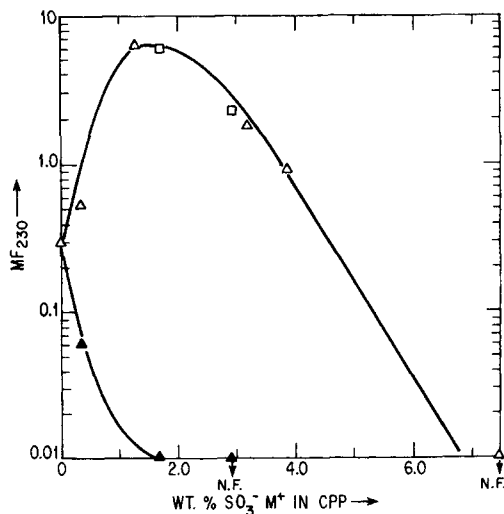


Fig. 5. Melt flow behavior of polypropylene metal sulfonates, CPP(SO₃⁻M⁺): (Δ) CPP(SO₃⁻Na⁺); (□) CPP(SO₃⁻K⁺); (▲) CPP(SO₃⁻Na⁺) + ~0.5% NaOH. CPP = crystalline polypropylene.

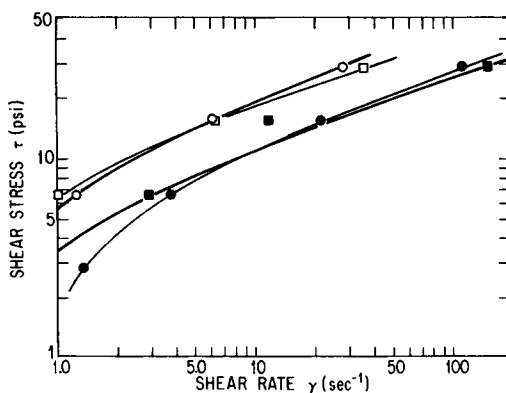


Fig. 6. Melt viscosity of sodium hydroxide containing polypropylene sodium sulfonate, CPP ($\text{SO}_3^- \text{Na}^+$), compared to polypropylene: CPP(0.3 wt-% $\text{SO}_3^- \text{Na}^+$) + 0.5 wt-% NaOH at 190°C (○) and 230°C (●); CPP at 190°C (□) and 230°C (■).

TABLE IV
Nucleation Data on Selected Polypropylene Samples

Sample	$\text{SO}_3^- \text{Na}^+$, wt-%	$\text{Na}^+ \text{OH}^-$, wt-%	T_c , °C
Homopolymer	none	none	117
	none	0.5	116
	0.4	none	117
	3.0	none	120
	0.4	0.2	125
	3.0	3.0	125
Propylene-ethylene copolymer	none	none	120
	none	0.5	120
	0.4	none	120
	0.4	1.0	130

DISCUSSION

In order to produce a chlorosulfonation product stable at the melt temperature of polypropylene, it is necessary to keep the chlorine content low (Fig. 1) and to completely react all sulfonyl chloride groups to a thermally stable form (i.e., metal sulfonate) [cf. Table III]. A low chlorine content with reasonable levels of metal sulfonate in the polymer requires that the $\text{SO}_2\text{Cl}/\text{Cl}$ ratio in the initial chlorosulfonation reaction be as high as possible. In confirmation of previous work,⁶ we find that low reaction temperature and high SO_2/Cl_2 ratio in the feed gas favor high ratios of $\text{SO}_2\text{Cl}/\text{Cl}$ in the product (Table II, Figs. 2 and 3). In addition, carbon tetrachloride is more desirable as vehicle than either benzene or carbon disulfide.

Dependence of the $\text{SO}_2\text{Cl}/\text{Cl}$ ratio on vehicle and temperatures probably derives from the reversibility of the step,

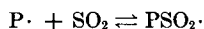


TABLE V
Mechanical Property Data on Selected Injection-Molded Specimens

Property	Polypropylene				Propylene-ethylene copolymer				
	HP(1) (SO ₂ -Na ⁺)	HP(1) (SO ₂ -Na ⁺) + NaOH	HP(1) (SO ₂ -Na ⁺)	HP(2) (SO ₂ -Na ⁺) + NaOH	HP(2)	COP-1 (SO ₂ -Na ⁺)	COP-1 (SO ₂ -Na ⁺) + NaOH	COP-2 (SO ₂ -Na ⁺)	COP-2 (SO ₂ -Na ⁺) + NaOH
SO ₂ -Na ⁺ wt-%	none	5.80	0.32	none	none	none	0.39	0.16	0.64
NaOH, wt-%	none	none	0.68	none	1.00	none	none	0.18	0.40
MF ₂₀₀	0.3	<0.01	0.06	3.0	0.10	3.9	3.5	2.3	3.9
Flex modulus × 10 ⁻³ , psi	195	168	214	200	232	137	143	155	143
Tensile at yield, psi	6067	—	7010	5104	6070	4084	4000	4073	3582
Elong. at yield, %	25.0	—	42.0	14.1	28.1	12.0	14.0	16.7	8.8
Room-temp. notched Izod, ft.-lb./in. notch	2.2	3.1	5.3	1.5	1.3	3.0	4.8	2.7	4.7
Unnotched Izods at: 0°F	5.0	8.6	7.5	9.1	7.2	NB	—	NB	36.9
-20°F	5.1	9.5	6.7	5.7	6.1	21.2	27.1	37.2	27.9
-40°F	5.2	—	8.6	5.7	6.2	22.5	14.8	19.9	24.4
Cryst. half-time at 130°C, min	3.1	—	0.5	11.4	0.6	5.6	—	1.8	5.9
T _g , °C	118	118	124	117	126	120	120	122	120

^a All runs at SO₂/Cl ratio = 2.5/1, temperature = 5°C, ∴ molar ratio SO₂-Na⁺/Cl ≈ 0.8 (cf. Tables II and III).

NOTE: HP(1) and HP(2) are different grades of homopolypropylene. COP-1 and COP-2 are two different lots of the same grade of impact propylene-ethylene copolymer.

TABLE VI
Mechanical Property Data on Selected Compression-Molded Specimens

Property	Polypropylene ^a		Propylene-ethylene copolymer ^a			
	HP(2)	HP(2) (SO ₃ ⁻ Na ⁺) + NaOH	COP-1	COP-1 (SO ₃ ⁻ Na ⁺) + NaOH	COP-2	COP-2 (SO ₃ ⁻ Na ⁺) + NaOH
1% tensile sec. mod. × 10 ⁻³ , psi	135.0	163.2	99.4	113.5	100.6	119.6
Tensile at yield, psi	4790	5066	2654	3024	—	—
Burst strength kg-cm/mil, at:						
23°C	0.61	0.36	3.96	3.20	—	—
-17°C	—	—	2.97	3.37	—	—

^a Sample components as shown in Table V.

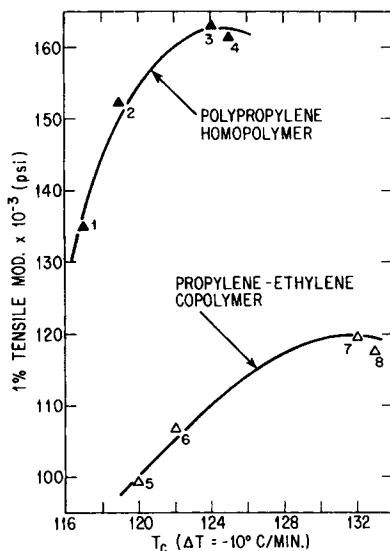


Fig. 7. Effect of sodium hydroxide concentration on modulus, crystallization temperature, and melt flow of two sodium sulfonate-containing polypropylenes. Concentrations in wt-%.

Homopolymer		Copolymer	
(1) [SO ₃ ⁻ Na ⁺] = 0, [NaOH] = 0, MF = 3.0	(5) [SO ₃ ⁻ Na ⁺] = 0, [NaOH] = 0, MF = 3.9	(2) [SO ₃ ⁻ Na ⁺] = 1.7, [NaOH] = 0.5, MF = 1.5	(6) [SO ₃ ⁻ Na ⁺] = 0.7, [NaOH] = 0.2, MF = 2.4
(3) [SO ₃ ⁻ Na ⁺] = 1.7, [NaOH] = 1.0, MF = 0.1	(7) [SO ₃ ⁻ Na ⁺] = 0.7, [NaOH] = 0.4, MF = 0.10	(4) [SO ₃ ⁻ Na ⁺] = 1.7, [NaOH] = 2.0, MF = 0.04	(8) [SO ₃ ⁻ Na ⁺] = 0.7, [NaOH] = 0.8, MF = 0.06

MF = melt flow at 230°C

where $P\cdot$ = polymeric radical. Temperature dependence of the relative rates for this type of reaction are known⁷ to depend on the degree of substitution of the polymer radical involved, i.e.,

<u>Copolymerization of SO₂ and</u>	<u>Ceiling temp.</u>
C ₂ H ₄	156°C
C ₃ H ₆	88°C
<i>i</i> -C ₄ H ₈	4°C

In the case of polypropylene, the polymer radical involved may be primary, secondary, or tertiary, depending on the point of attack by the chlorine atom. It is well known^{8,9} that the vehicle has a pronounced effect on the selectivity of chlorine atom attack on hydrocarbons. Vehicles which tend to coordinate the chlorine radical (i.e., benzene and carbon disulfide) favor attack at the *tert*-hydrogen position. Reaction of the polymeric radical thus formed with sulfur dioxide produces the thermally unstable polymer sulfoxy radical which can dissociate before abstracting a chlorine to renew the chain. Consistent with this reasoning, it is found that high SO₂Cl/Cl ratios in the product are favored by use of CCl₄ as vehicle (nonselective toward attack at the *tert*-hydrogen position) and by low temperatures (to prevent breakdown of P—SO₂· prior to chlorine abstraction).

The desirable mechanical properties of polypropylene derive largely from its high crystallinity. In order to preserve this crystalline fraction, chlorosulfonation of the powder was done in slurry. X-Ray crystallinity data on the product powders indicates that the reaction occurred almost exclusively in the amorphous phase (Fig. 4); hence, the material might be viewed as a block copolymer of polypropylene and chlorosulfonated polypropylene. On conversion to the sodium sulfonate form, melting, and re-solidifying, the crystallinity (as estimated from IR) is somewhat reduced because isotactic portions of the polymer chains which were in the amorphous phase have now been rendered noncrystallizable by the chlorine and sodium sulfonate groups. The deleterious effect on crystallinity is kept to a minimum by blocking in the modifying groups as opposed to random placement.

The properties of the modified polypropylenes were determined after conversion to their sodium sulfonate form. These properties were found to depend strongly on both the level of sodium sulfonation of the polymer and on the concentration of sodium hydroxide (Fig. 7). The free-radical chlorosulfonation step results in some molecular weight breakdown as evidenced by the increasing melt flow of the sodium sulfonate form (Fig. 5). Figure 5 includes a pair of cases where the sodium was ion exchanged with potassium; the potassium form showed essentially the same melt flow behavior as the sodium form. At fairly low levels of sodium sulfonation, associations of the ionic groups compensate for the molecular weight breakdown, and the melt flow values turn downward. In the presence of 0.5 wt-

% sodium hydroxide, the melt flow of the materials decreases continuously; and at $\sim 2.0\%$ $\text{SO}_3^- \text{Na}^+$, they show essentially no flow with the 2.16-kg weight. There is little difference in the shear-stress, shear-rate dependency for the modified polymer (containing an included sodium hydroxide phase) as against homopolypropylene of equivalent starting melt flow over the range of conditions explored (Fig. 6).

It appears from the DSC crystallization temperature data that the presence of sodium sulfonate groups in polypropylene may cause some enhancement of the nucleation rate, but the most dramatic effect is shown by the combination of polypropylene sodium sulfonate and an included sodium hydroxide phase (Table IV). Added sodium hydroxide alone has no measurable effect on the nucleation rate in the concentration range of interest.

The data on melt flow behavior and nucleation rate support a picture of ionic association which persists above the melting point of crystalline polypropylene. In the presence of an included sodium hydroxide phase, the polymer sodium sulfonate groups appear to interact with the ionic surface of the included phase such as to cause some ordering of the polymer chains even above the nominal melting point of polypropylene. The interaction is presumed to involve a partial ion exchange between phases. These ordered regions can serve as crystallization nuclei¹⁰ which cause formation of many small crystallites on cooling. In the temperature and shear range studied in this work, the ionic associations are essentially irreversible (Fig. 6).

Mechanical property data (Tables V and VI) are consistent with expectation^{5,12} for highly nucleated crystalline polypropylene, that is, an improved modulus and yield strength with little or no effect on Izod impact strength. It should be noted that in the absence of an included sodium hydroxide phase, even high levels of sodium sulfonate in the polymer do not give the desirable balance of mechanical properties (cf. Table V, HP(1), $\text{SO}_3^- \text{Na}^+$).

SUMMARY AND CONCLUSIONS

Crystalline polypropylene sodium sulfonates have been prepared by the light-initiated chlorosulfonation of polypropylene followed by treatment with hot aqueous sodium hydroxide. Chlorination during the chlorosulfonation reaction is minimized by the use of a high SO_2/Cl_2 ratio, low temperature, and a nonselective vehicle.

Maximum retention of crystallinity of the polypropylene is obtained by conducting the chlorosulfonation in slurry rather than in solution so that the long isotactic sequences contained in the crystalline phase are protected from the reaction.

Polypropylene sodium sulfonates are found to interact with an included sodium hydroxide phase as evidenced by melt flow behavior, nucleation rate, and mechanical properties. The interaction apparently involves a

partial ion exchange between phases with resultant ordering of polymer chains above the nominal melting point of the polypropylene.

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