The Preparation and Thermodynamic Behaviors of Chlorosulfonated Polyethylene

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ABSTRACT: The chlorosulfonated polyethylene (CSM)s with different content of chlorine and sulfur elements were prepared by aqueous solution suspension method. Prepared CSMs were characterized by Fourier transform infrared (FTIR) spectra. The content of chlorine and sulfur elements of CSM was confirmed by ion chromatography. The thermal properties and crystallization behaviors of the prepared CSMs were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. In each TGA curve, one can observed two distinct weight loss steps, and the degradation temperatures decreased with the content of chlorine and sulfur elements increasing. The degradation temperatures of all the prepared CSMs exceeded 170°C in air, which showed good thermal stability. The calculated Avrami exponent by the БорохобскИЙ nonisothermal crystallization kinetics equation was nearly 4, which proved the CSM was homogeneous nucleation with a three-directional spherulitic growth. The WAXD results indicated that the crystallinity of CSM decreased with the increment of chlorine and sulfur content. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2095–2100, 2010

Key words: chlorosulfonated polyethylene; DSC; crystallization kinetics

INTRODUCTION

As one of special synthesized rubber widely used in engineering field, the chlorosulfonated polyethylene (CSM)s are well-known for having excellent thermal and mechanical properties as well as being resistances to oxidation and having chemical stability under acidic and basic conditions. CSM are extensively applied to some areas, such as, single-ply roofing membrane, wire and cable jacketing, coupling agent, and wiring.[1–5] The CSM may be obtained by solution method, gas–solid method, and aqueous solution suspension method. At present, Dupont and Jilin petrochemical company produced CSM via solution method in CCl_4 solvent. The CCl_4 has been prohibited because it is one of a series of ozone depleting gas. There are no other reasonable solvents were used to prepare CSM by solution method in literature. Therefore, the development of CSM becomes slow. There are many patents available on preparation of CSM by gas–solid method using polyethylene (PE) and a gaseous mixture of chlorine and sulfur dioxide. The U.K. patents and the Beijing University of Chemistry have reported the gas–solid method using chlorination polyethylene (CPE) as the material, which could resolve the environmental pollution problem.[6] The CPE decreases the reaction activity due to the chemistry and space steric hindrance. Moreover, it is difficult to dissipate producing heat during the reaction, so that the gas–solid method has not been used in industrial production.

As one of engineering materials, the performance of CSMs should be closely related to their internal structure, especially crystallization process during the production and processing of CSM. To obtain materials with better physical properties and get the optimum conditions in an industrial process, it is necessary to compare the nonisothermal crystallization behaviors of different polymer systems.

In this article, the CSMs with different chlorine and sulfur content were prepared by aqueous solution suspension method. To obtain more detailed information about the crystallization and degradation behaviors, the nonisothermal crystallization and thermal degradation behaviors of CSM with different chlorine and sulfur content were discussed in detail.
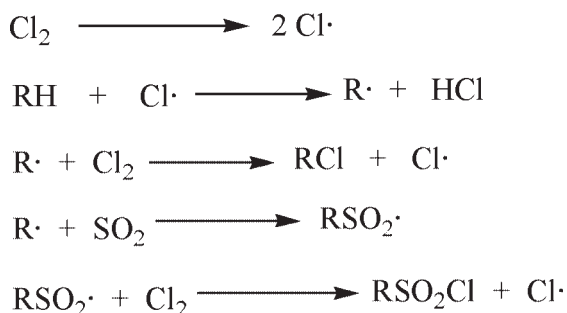
Correspondence to: H. X. Zhang (zhanghx@mail.ccut.edu.cn).

EXPERIMENT

Materials

Linear low density polyethylene (LLDPE) was supplied by Jilin petrochemical company, China.

$$Cl_2 \longrightarrow 2\,Cl\cdot$$

$$RH \;+\; Cl\cdot \longrightarrow R\cdot \;+\; HCl$$

$$R\cdot \;+\; Cl_2 \longrightarrow RCl \;+\; Cl\cdot$$

$$R\cdot \;+\; SO_2 \longrightarrow RSO_2\cdot$$

$$RSO_2\cdot \;+\; Cl_2 \longrightarrow RSO_2Cl \;+\; Cl\cdot$$

Scheme 1 The reaction mechanism of CSM.

Chlorine and sulfur dioxide gaseous mixture (1 : 1) were obtained from Changchun Xinguang gaseous company. Polyvinyl alcohol (PVA), azobisiso butyronitrile (AIBN), and hydroxypropyl cellulose (HPC) were supplied by Beijing Organic Chemical Plant and used without further purification.

Preparation of chlorosulfonated polyethylene

The CSMs with different chlorine and sulfur content were prepared by aqueous solution suspension process with LLDPE. The schematic reaction is shown in Scheme 1. Polymerization reaction was carried out in a 500-mL four-neck round-bottom flask with two atmosphere inlet, a mechanical stirrer and a thermometer inlet. The PVA and HPC were stirred and well-dispersed in the water for some time. When the temperature of reaction mixture was heated to 85°C, the Cl_2 was fed into the reaction system and then the initiator AIBN was dipped into the flask. After a desired period, the gaseous mixtures of chlorine and sulfur dioxide (1 : 1) were simultaneously fed into the reaction system. The reaction was ended by blowing the dry nitrogen into the reaction system. The residual gaseous mixtures were absorbed by 2 mol/L $NaHSO_3$ and 2 mol/L NaOH solutions. The precipitated CSMs polymers were washed by boiling water for several times and dried in a vacuum oven at 80°C for an additional day.

Characterization of CSM

The Fourier transform infrared (FTIR) spectrums of prepared CSM samples were recorded by Avatar-360 FTIR spectrometer. The content of chlorine and sulfur elements in CSM was calculated using ion chromatograph Dionex-2010I (Dionex, Sunnyvale, CA) comprised of a GP50 gradient pump and an ED 40 conductivity detector. Anions were determined on an IonPac AS9-HC (2 mm × 250 mm) anion exchange column using 9.0M Na_2CO_3 eluent at 0.25 mL/min and suppressed conductivity detection with ASRC®-ULTRA suppressor (2 mm) in recycle mode,

TABLE I
Elemental Analysis Data of CSM

Samples	Cl (wt %)	S (wt %)
CSMa	30	1.13
CSMb	28	0.62

50 mA. Thermogravimetric analyzer (TGA) Pyris Perkin-Elmer TGA-7 was used to study the thermal properties of the CSM. A total of ~ 5 mg of CSM samples were heated to 110°C and kept at this temperature for 20 min to remove any residual water and solvent. Subsequently, the samples were cooled to 50°C and then reheated to 600°C at a rate of 10°C/min in air. The crystallization behaviors of CSM were carried out by differential scanning calorimeter (DSC) DSC-7 Perkin-Elmer. Atotal of ~ 5 mg of CSM samples were sealed in aluminum pans and placed in the nitrogen atmosphere. They were rapidly heated to 110°C at a rate of 20°C/min and kept at this temperature for 5 min to remove moisture and eliminate the effects of the thermal history. Then, the samples were cooled to 50°C at four different cooling rates of 4°C/min, 6°C/min, 8°C/min, 10°C/min, and 12°C/min, respectively. The crystalline structure of the CSM samples was studied by X-ray diffraction. Wide-angle X-ray diffraction patterns were obtained using a Rigaku D/MAXPC 2200 diffractometer and monochromatic Cu Kα radiation, and a rotating-anode generator operated at 30 kV and 40 mA. The diffractograms were scanned in the 2θ range from 5° to 40°.
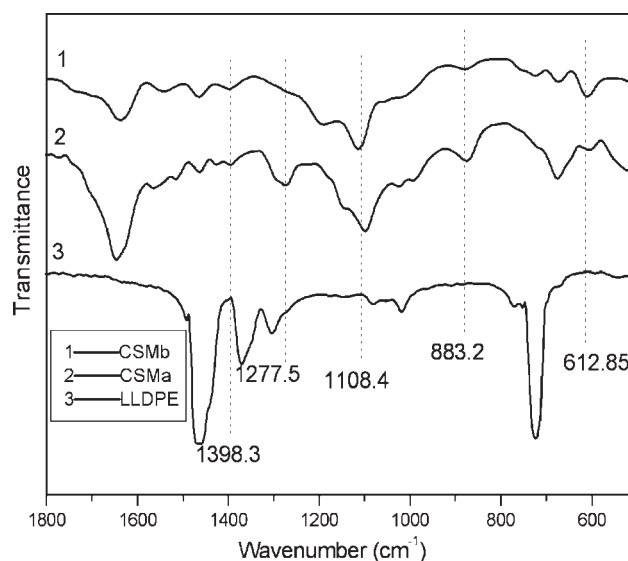

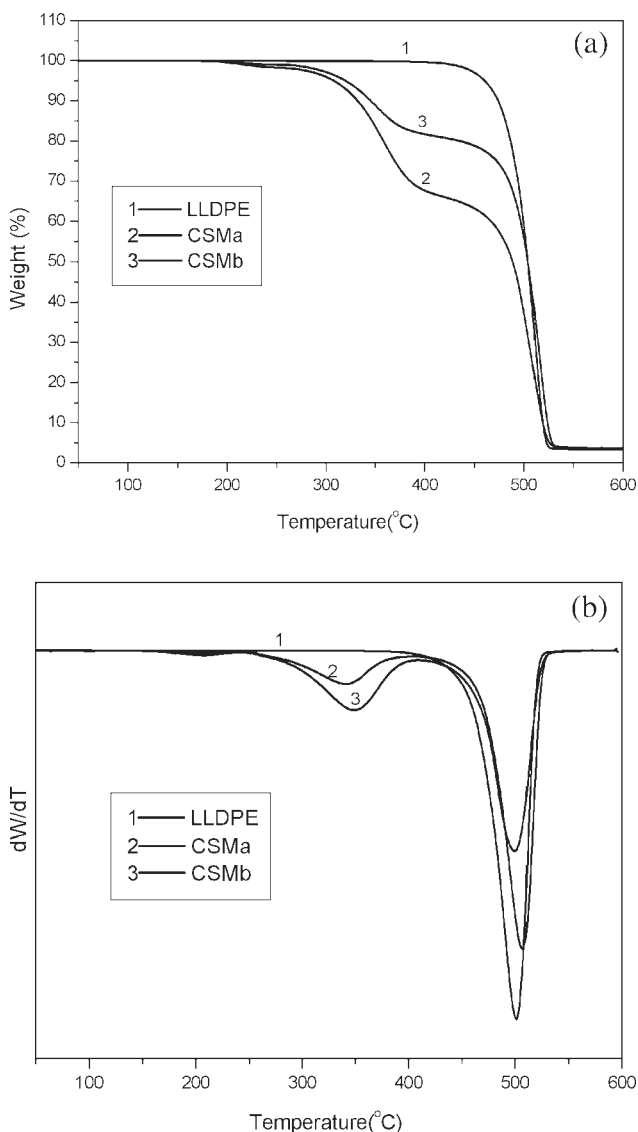**Figure 1** The FTIR spectra of CSM (1-CSMb, 2-CSMa, and 3-LLDPE).

Figure 2 TGA and DTG curves for CSM.

Figure 3 The DSC curves of CSMa (a) and CSMb (b) cooled from the melt at various cooling rates.

RESULTS AND DISCUSSION

Preparation and characterization of CSM polymers

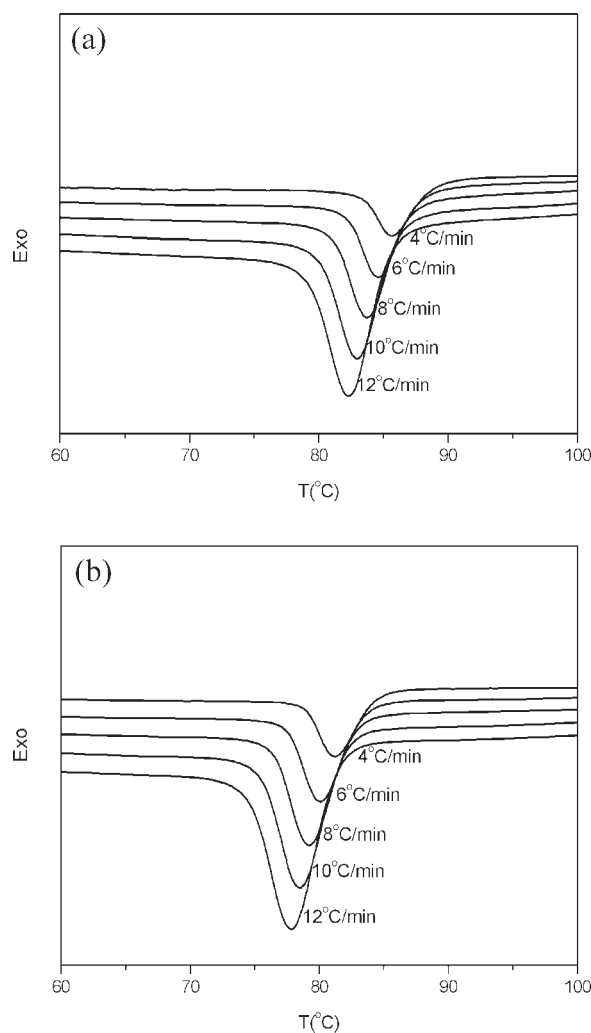The CSM polymers with different content of chlorine and sulfur elements were prepared by aqueous solu-tion suspension. The reaction mechanism is shown in Scheme 1.

The chlorine and sulfur content of prepared CSM was calculated by ion chromatography. The analysis results are displayed in Table I. It can be seen that the chlorine and sulfur elements were introduced

TABLE II
The Nonisothermal Crystallization Kinetics Data of CSM

Cooling rate (°C/min)	Samples			
	CSMa		CSMb	
	$T_p{}^a$ (°C)	$T_{1/2}{}^b$ (s)	$T_p{}^c$ (°C)	$T_{1/2}{}^d$ (s)
4	85.67	128.23	81.17	64.91
6	84.55	83.43	80.08	61.65
8	83.72	51.11	79.21	52.78
10	82.90	45.05	78.44	51.69
12	82.36	30.21	77.77	42.49

[a,c]Maximum crystallization rate temperature.
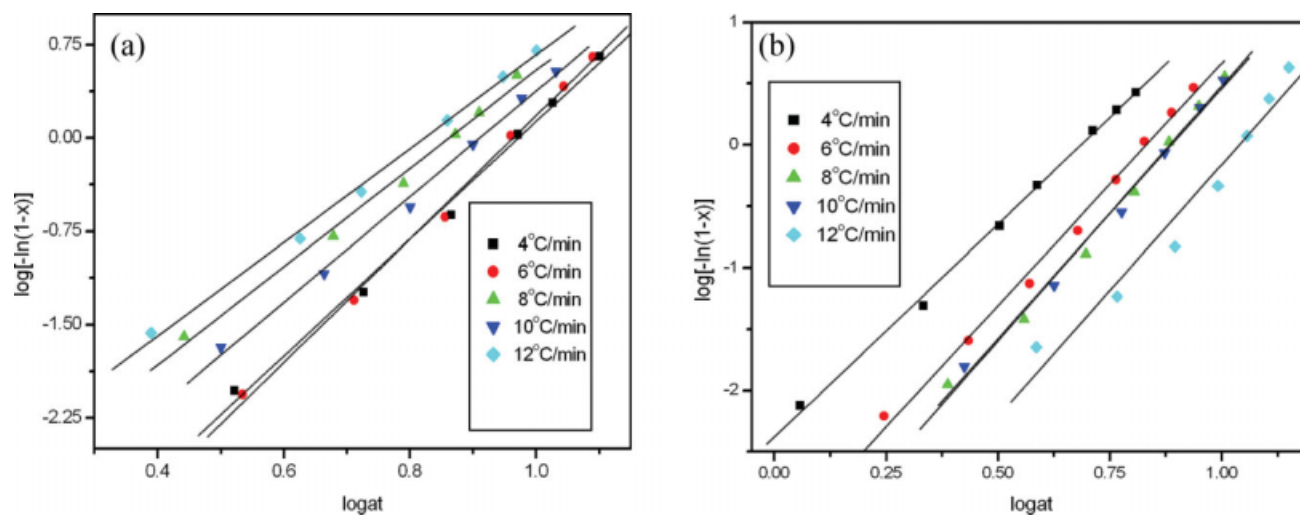[b,d]The semi-life crystallization time.

Figure 4 Plots of nonisothermal crystallization kinetics (a-CSMa and b-CSMb). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

into the polymers, and the content increased with the increment of the time of Cl_2 and SO_2 feeding into flask. The CSM with 30% chlorine and 1.13% sulfur was defined as CSMa, whereas the CSM with 28% chlorine and 0.62% sulfur was defined as CSMb.

The successful introduction of —SO_2Cl groups to the polymer was confirmed by FTIR spectra,[7] as shown in Figure 1. Two absorption bands at 1108.4 cm^{-1} and 1398.3 cm^{-1} are characteristic peaks of —SO_2Cl present in CSM. The —Cl groups are observed at 612.85 cm^{-1} and —CH_2 groups bending vibration are found at 1277.5 cm^{-1}. These results confirmed that the —SO_2Cl groups were surely incorporated into the copolymers as expected.

Thermal properties of CSM

The thermal properties of the modified PE by chlorination and chlorosulfonation have been widely studied by TGA instruments.[8–11] In this work, the thermal behaviors of CSM with different chlorine and sulfur content were carried out by TGA. The TGA curves and the corresponding derivative thermogra-

vimetric (DTG) curves of CSM and LLPE are shown in Figure 2(a,b). The degradation of CSM underwent two weight loss steps and DTG curves of LLPE displayed only one transition step. On the TGA curves of CSM, the slight weight loss between 170°C and 240°C were mainly caused by the dehydrochlorination of CSM, which was similar with the decomposition of PVC.[12,13] The distant weight loss around 285°C were mainly associated with the degradation of dehydrochlorinated residues and the splitting-off —SO_2Cl groups of CSM.[9] The second step weight loss beginning at 450°C was attributed to the decomposition of the main chain of CSM,[9] which was accordant with the decomposition temperature of main chain of LLPE. Moreover, CSMa was observed to have lower $T_{d5\%}$ (temperature of 5% weight loss, 307°C) than that (320°C) of CSMb. It was observed from DTG curves [Fig. 2(b)] that the degradation maximal rate of CSMa corresponding first step weight loss temperature (341°C) was shifted to the higher temperature (350°C) for CSMb. All these results illustrated that the thermal stability of CSM decreased with increasing of the chlorine and sulfur content. However, it is important to note that all

TABLE III
The Parameters of Nonisothermal Crystallization Kinetics of CSM

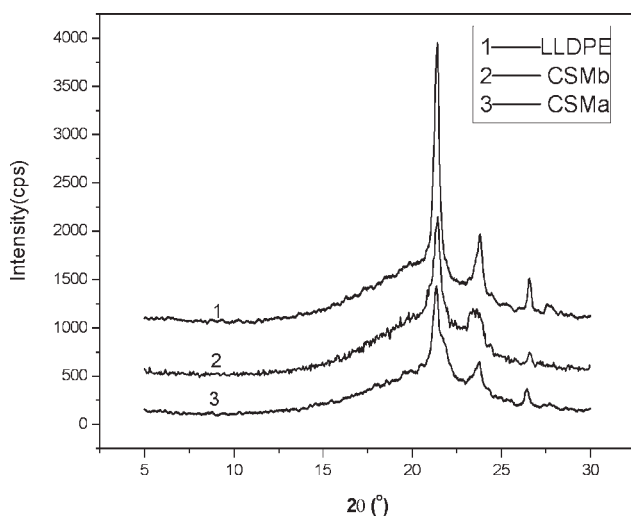| Sample	Parameters	Cooling rate (°C/min)				
		4	6	8	10	12
CSMa	n	4.71	4.38	3.95	4.25	3.77
	lgZ	−4.64	−4.78	−3.48	−3.55	−3.10
	Z	2.29×10^{-5}	1.66×10^{-5}	3.31×10^{-4}	2.82×10^{-4}	7.94×10^{-4}
CSMb	n	3.47	3.94	4.15	4.08	4.12
	lgZ	−2.38	−2.94	−3.25	−3.38	−4.27
	Z	4.17×10^{-3}	1.15×10^{-3}	5.62×10^{-4}	4.17×10^{-4}	5.37×10^{-5}

Figure 5 The WAXD curves of CSMa, CSMb, and LLDPE.

temperatures of weight loss of CSM are higher than 170°C, which meet thermal requirement of CSM as functional materials.

The crystallization behavior of CSM

The DSC instrument has been widely used to investigate the crystallization behavior of modified PE.[14–16] The nonisothermal crystallization DSC curves of the CSM at four cooling rates are shown in Figure 3. The parameters are listed in Table II. From the results of DSC profiles (Fig. 3), we can see clearly that the exothermic peak widens and shifts to a lower temperature region with the cooling rate increasing. As expected, the data of Table II show that the semi-crystallization time decreased with cooling rate increasing as well as the maximum crystallization rate temperature (T_p) of CSMa was higher than that of CSMb at the same of cooling rate. It may be explained that the cooling rate increasing, the activities capacity of the molecular chain is limited, which makes the rule alignment of the molecular chain become worse at a comparatively low temperature. It induces that crystal form is more imperfect and nucleation is lag.

Nonisothermal crystallization kinetics of CSM

In this work, the Бороховский theory[17] was used to study the nonisothermal crystallization kinetics. The Бороховский equation is defined as following:

$$X = 1 - \exp[-Z(\text{at})^n] \tag{1}$$

Double logarithming eq. (1), we can obtain eq. (2):

$$\lg[-\ln(1-X)] = \lg Z + n\lg(\text{at}) \tag{2}$$

where n is the mechanism constant that can be obtained from the slope of the curves of nonisothermal crystallization kinetics, Z is the crystallization rate constant, $\lg Z$ is the intercept. The $\lg[-\ln(1-X)] \sim \lg(\text{at})$ double logarithmic curves for each cooling rate are shown in Figure 4. Each curve shows an almost linear relationship. The exponent n depends on the type of nucleation and the growth dimension.[18] It indicates that the Avrami equation can properly describes the isothermal crystallization behaviors of the samples. From the slopes and intercepts of the lines, the Avrami exponent n and the crystallization rate Z can be obtained. The results are shown in Table III. The average values of the Avarami exponent n of CSMa and CSMb samples are 4.212 and 3.952, respectively. In the Avrami expression, the Avrami exponent n provides qualitative information on the nature of nucleation and the growth process. The Avarami exponent n of CSM samples is nearly 4, which illuminates homogeneous nucleation with a three-directional spherulitic growth.[19] In addition, the average crystallization rate constant increases from 2.89×10^{-4} of CSMa to 12.7×10^{-4} of CSMb. All the parameters of crystallization kinetics could explain well the nucleation and growth mechanism of the CSM.

The crystallinity of CSM

The crystallinity of polymers has significant effects on its mechanical performance.[20,21] In this work, X-ray diffraction was performed to evaluate the degree of crystallization of the CSM. X-ray diffractograms of the CSM are displayed in Figure 5. The crystallinity (%) is listed in Table IV. As seen in Figure 5, all

TABLE IV
The Analytic Data of CSM

Samples	T_d (°C) extrapolated onset for first weight loss	T_d (°C) extrapolated onset for second weight loss	Crystallinity (%)
CSMa	279	427	16.26
CSMb	284	432	21.02
LLDPE	359	–	55.00

CSM samples exhibit one small crystalline peak, which indicates small crystalline structure exists in the CSM. It can be observed that the diffraction intensity decreased after the chlorine and sulfur elements were introduced into the polymers. Moreover, the crystallinity of CSM decreased with the increment of chlorine and sulfur elements content. For example, the crystallinity of CSM increased from 16.26% of CSMa to 21.02% of CSMb as well as was <55.00% of LLDPE. It is because that the —Cl and —SO$_2$Cl groups are polar groups, which can hinder molecular internal rotation and also enhance intermolecular interaction. So the crystallization ability of CSM decreases.

CONCLUSIONS

In this work, the CSM polymers with different content of chlorine and sulfur elements were successfully prepared by an aqueous solution suspension method. The successful introduction of —Cl and —SO$_2$Cl groups to the polymers was confirmed by FTIR spectra and ion chromatography. TGA results showed that CSM had very good thermal stability and decreased with content of chlorine and sulfur elements of CSM increasing. DSC results indicated that the exothermic peak widened and shifted to a lower temperature region with the increment of cooling rate. The calculated Avrami exponent from DSC results was nearly 4, which proved that the CSM was homogeneous nucleation with a three-directional spherulitic growth. X-ray diffractograms revealed that with the increment of chlorine and sulfur elements content, the crystallinity of CSM

decreased. The crystallization rate constant increased from 2.89×10^{-4} of CSMa to 12.7×10^{-4} of CSMb.

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