Relationship of the Sequence Distribution of a Polymer to the Catalytic Activity of Its Nd Complex

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RELATIONSHIP OF THE SEQUENCE DISTRIBUTION OF A POLYMER TO THE CATALYTIC ACTIVITY OF ITS Nd COMPLEX

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ABSTRACT

The sequence distribution of the monomeric units in the styrene-acrylic acid copolymer has been obtained by calculation. The probability of long sequences of styrene increases with an increase in the content of the monomer in the copolymer. The highest distribution of short sequences of styrene takes place for the copolymer containing equimolecular amounts of styrene and acrylic acid. The copolymer which has this latter structure is inadequate for the synthesis of highly active supported complexes. When the distributions of long and short sequences of styrene are approximately equal, the activity of the Nd and Fe prepared polymer complexes is higher.

INTRODUCTION

Metal (Fe, Nd) complexes supported on polymers show high catalytic activity and stereospecificity in the polymerization of conjugated dienes [1, 2]. It is well known that the number of vacant sites on active metal ions and the distribution of electron density of the metal ions, i.e., bond polarity and bond strength of the coordination complex, can be changed by varying the ligands coordinated to it and the type of aluminum alkyl

used. The latter also influences the activity and stereospecificity of the
catalyst thus prepared. The covalency of the metal-oxygen bonds in the
polymer-supported neodymium complexes possessing the bidentate car-
boxylate structure makes the exchange reaction to form the active centers
easier [3]. The details of the effect of the polymeric ligand is not well
understood. When the polymer is substituted for low molecular weight
ligands, a single and regular factor evolves into multiple and variable
factors. Such is the case of the effect of ligand coordination on the
catalytic activity of rare earth metal ions. The sequence distribution of
monomeric units in styrene–acrylic acid copolymer and its relationship to
catalytic activity have been studied from the perspective of polymer struc-
ture in this paper. The poorest activity of the neodymium complex sup-
ported on styrene–acrylic acid copolymer takes place for the copolymer
containing the highest distribution of short sequence of styrene. In the
case of the equal distribution of long and short sequences of styrene, the
catalytic activity of the neodymium complex is higher.

EXPERIMENTAL

Materials

Chemically pure grade benzyl chloride was distilled before use. The
phenanthroline (Phen.) concentration used was 10 μmol/mL toluene.
Analytically pure grade toluene was refluxed with a K-Na alloy and dis-
tilled before use. Commercially pure grade hexane was dried over active
alumina for a week. Neodymium chloride was prepared according to the
literature [4]. Triisobutylaluminum and diethylaluminum chloride were
obtained from Fluka AG. Butadiene was dried over active alumina before
use. Ethylene–acrylic acid copolymer (EAAC) was obtained from Poly-
sciences, Inc., Warrington, Pennsylvania.

The styrene (S)–acrylic acid (AA) copolymer (SAAC) was prepared
according to the literature [5]. The amount of tetrahydrofuran (THF)
used as solvent was maintained at a AA/THF molar ratio of 1. The
conversion was about 10%. The reactivity ratios r_1 and r_2 of styrene and
acrylic acid determined by the Fineman-Ross method [6] were 0.23 and
0.15, respectively. Polystyrene-*graft*-polyacrylic acid (PS-*gr*-PAA) and
polypropylene-*graft*-polyacrylic acid (PP-*gr*-PAA) were prepared accord-
ing to the literature [7]. The carboxylic acid content of the copolymer was
determined by titration.

The synthesis of the polymer-supported metal complexes (SAAC ·
Nd, EAAC · Nd, PS-*gr*-PAA · Nd, PE-*gr*-PAA · Nd, and SAAC · Fe),

the determination of the quantity of bound metal in the complexes, and the microstructure of the polybutadiene produced were carried out according to previously reported methods [1, 2].

RESULTS AND DISCUSSION

Sequence Distribution of the Monomeric Units in Styrene–Acrylic Acid Copolymer

Mayo-Lewis's equation [8], which relates the copolymer composition to the monomer composition, is given by

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad \left(= \frac{m_1}{m_2} \text{ for low conversions} \right)$$

where M_1 and M_2 refer to the monomer composition, m_1 and m_2 refer to the polymer composition, and r_1 and r_2 refer to the reactivity ratio of M_1 and M_2, respectively. According to statistical theory, the probability that a sequence of m_1 units contains n members is

$$P(m_1)_n = P_{11}^{(n-1)}(1 - P_{11}) = \left(\frac{1}{1 + \dfrac{1}{r_1 F}} \right)^{n-1} \frac{1}{1 + r_1 F}$$

Similarly:

$$P(m_2)_n = P_{22}^{(n-1)}(1 - P_{22}) = \left(\frac{1}{1 + \dfrac{F}{r_2}} \right)^{n-1} \frac{1}{1 + \dfrac{r_2}{F}}$$

These values represent the fraction of all the m_1 sequences (or m_2, respectively) formed by n members, where F, which is a function of the ratio (f) between the molar concentration of m_1 and m_2 in the copolymer, can be obtained from the copolymerization equation written by Fineman and Ross [6]:

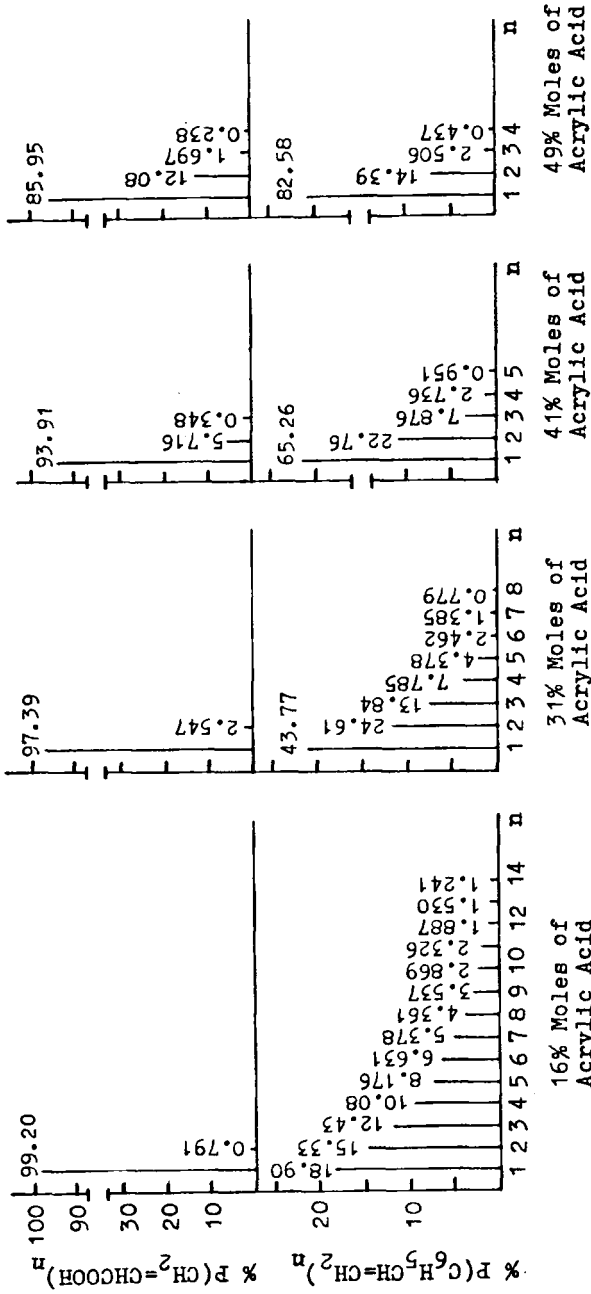$$F = \frac{f - 1 + \sqrt{(f - 1)^2 + 4r_1 r_2 f}}{2r_1}$$

FIG. 1. Distribution function of sequences of different lengths in SAAC having different compositions.

TABLE 1. Distribution Function of Sequences of Different Lengths in SAAC Having Different Compositions[a]

M_s in SAAC, mol%	Percent $P(m_s)_n$										$n \geq 15$
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$		
84	18.90	15.33	12.43	10.08	8.176	6.631	5.378	4.361	3.537	for n between 10 and 14, $P(m_s)_n = 9.853\%$	1.006
74	34.53	22.61	14.80	9.690	6.344	4.154	2.719	1.780	for n between 9 and 14, $P(m_s)_n = 3.112\%$		0.092
69	43.77	24.61	13.84	7.785	4.378	2.462	1.385	for n between 8 and 14, $P(m_s)_n = 1.748\%$			0.014
64	54.05	24.84	11.41	5.244	2.410	1.107	0.509	for n between 8 and 14, $P(m_s)_n = 0.431\%$			0.001
59	65.26	22.67	7.876	2.763	0.951	0.330	for n between 7 and 14, $P(m_s)_n = 0.176\%$				
51	82.58	14.39	2.506	0.437	0.076	for n between 6 and 14, $P(m_s)_n = 0.016\%$					

[a]Percent $P(m_s)n$ = percentage of sequences of styrene containing n monomer units. n = number of monomer units present in each sequence.

Figure 1 and Table 1 show the values of the distribution function P for sequences of different lengths for styrene–acrylic acid copolymers of different compositions. The probability of long sequences of styrene or acrylic acid increases with an increase of the content of the monomer in the copolymer. The highest distribution of short sequences of styrene occurs for the copolymer containing nearly equimolecular amounts of styrene and acrylic acid. In this case the values of the distribution function are about 85% for the alternating 1 : 1 sequence of both monomers. It seems that the monomers in the copolymer show a propensity for alternation. The distribution of long and short sequences of styrene is about equal for copolymers containing 64–69% mol styrene.

Relationship of the Sequence Distribution of the Monomeric Units in Styrene–Acrylic Acid Copolymer to the Catalytic Activity of the Polymer Complexes of Nd

The formulas of the support polymers of the neodymium complexes used in Table 2 are as follows:

$PS-CO_2H$ (PS)—(O)— $\underset{\underset{OH}{|}}{C}=O$ (V)
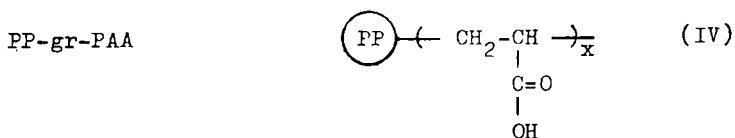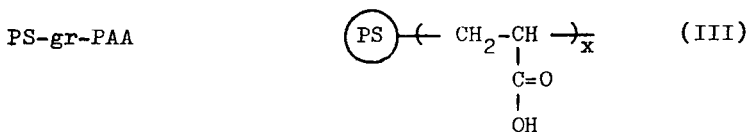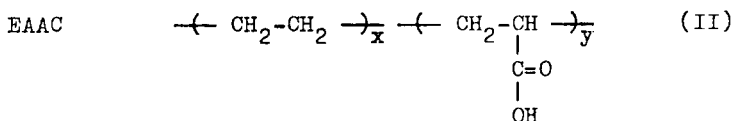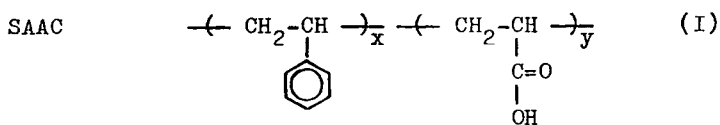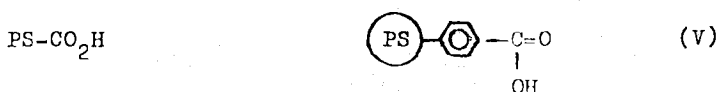
Different polymer-supported neodymium complexes have different cata-
lytic activities in the polymerization of butadiene despite the fact that the
support polymers each contain the same functional group, e.g., the car-
boxy group. For the grafted copolymers (III) and (IV), the sequence of
carboxy groups is equal to that of the homopolymer of acrylic acid. The
carboxy groups in the polymers (I) and (II) are bonded to the main chain
of SAAC (or EAAC). Polymers (V) and (VI) are different from polymers
(I) and (II), in that polymer (V) is carboxylated DVB-crosslinked poly-
styrene and polymer (VI) is carboxylated polyethylene. It is obvious that
the catalytic activity of the polymer-supported neodymium complexes
could be influenced by the arrangement of carboxy groups on the poly-
meric chain.

In order to determine the effect of the sequence distribution of the
monomeric units in SAAC on the catalytic activity of the SAAC · Nd
complexes, the quantity of bound Nd was controlled within a certain
range in the SAAC · Nd synthesis. For the copolymers with 26, 31, 33,
and 42% mol acrylic acid (Figs. 2e–h), the quantity of bound neodymium
in their metal complexes was approximately 0.52, 0.61, 0.66, and 0.66
mmol/g (Figs. 2a–d), respectively. It is seen from Fig. 2 that the activity
of polymer-supported neodymium complexes is related to the distribu-
tion function of sequences of the monomeric units in styrene–acrylic acid
copolymers. The lowest catalytic activity of the SAAC · Nd complexes
was observed for the polymer having the highest distribution of short
sequences of styrene. When the distribution of short sequences of styrene
is highest, both monomers in the copolymer show an increase in the
alternating arrangement. It may be suggested that in this case the average
distance between the carboxy groups is short in spite of the fact that they
are highly dispersed in the polymer. Thus the neodymium ions in the
complexes cannot readily come into contact with the organoaluminum
compound to form active centers. The nature of the Nd—O bond in PS-
gr-PAA · Nd, or in PP-gr-PAA · Nd, is similar to that in SAAC · Nd
and is highly covalent, but the polymer activity is quite different. It may
be seen that this difference is caused by the aggregation of the functional
groups on the polymer chain. The low activity for the neodymium com-

TABLE 2. Activity of Polymer-Supported Neodymium Complexes in Butadiene Polymerization

Complex	Quantity of bound metal, mmol/g	Nd/Bd, μmol/g	Cl/Nd, mol/mol	Al/Nd, mol/mol	Temperature, °C	Time, h	Conversion, %
SAAC · Nd[a]	0.67	0.3	3.5	200	50	6	94
EAAC · Nd[b]	0.44	0.3	3	200	50	6	96
Ps-gr-PAA · Nd[b]	0.30	0.3	3	200	50	6	Trace
PP-gr-PAA · Nd[c]	0.97	5	3	200	50	6	Trace
		mol/g					
(PS-CO2)3Nd[d]	0.86	25	2	40	70	48	44
(PE-CO2)2.5Cl0.7Nd[d]	0.22	100	2	40	100	10	25

[a]Third component, benzyl chloride; [b] and [d]third component, $Al(C_2H_5)_2Cl$; [c]third component, triphenylchloromethane; [a-d]cocatalyst, $Al(i\text{-}C_4H_9)_3$; [a-c]monomer concentration, 10 g/100 mL hexane; [d]Ref. 9.

FIG. 2. Distribution function of sequences of different lengths in SAAC having different compositions and activity of SAAC · Nd. Polymerization conditions: (a–d) Nd/Bd = 0.2 μmol/g; third component, Al(C$_2$H$_5$)$_2$Cl; Cl/Nd molar ratio = 3.5; cocatalyst, Al(i-C$_4$H$_9$)$_3$; Al/Nd molar ratio = 200; 50°C; 6 h.

Microstructure of polybutadiene, %

d

cis-1,4 43.9
1,2 55.5
trans-1,4 0.6

45

Fe = 0.62 mmol/g

c

cis-1,4 45.4
1,2 47.8
trans-1,4 6.8

89

Fe = 0.65 mmol/g

b

cis-1,4 49.8
1,2 43.8
trans-1,4 6.4

87

Fe = 0.66 mmol/g

a

cis-1,4 51.9
1,2 47.2
trans-1,4 0.9

83

Fe = 0.54 mmol/g

Conversion, %

h

94.94

60.69

23.86

4.801 0.570
9.378 1.449
3.687 0.243

1 2 3 4 5 6

n

39% Moles of Acrylic Acid

g

96.10

54.05

24.84

11.41
3.747 0.146
5.244 0.509
2.410 1.107

1 2 3 4 5 6 7

n

36% Moles of Acrylic Acid

f

97.39

43.77

24.61

13.84
2.547 0.779
7.785 1.385
4.378 2.462

1 2 3 4 5 6 7 8

n

31% Moles of Acrylic Acid

e

99.05

21.77

17.03
13.32
10.42
8.154 0.942
6.379 0.895
4.990 1.144
3.904 1.462
3.054 1.869
2.389

1 2 3 4 5 6 7 8 9 10 11 12 13 14

n

18% Moles of Acrylic Acid
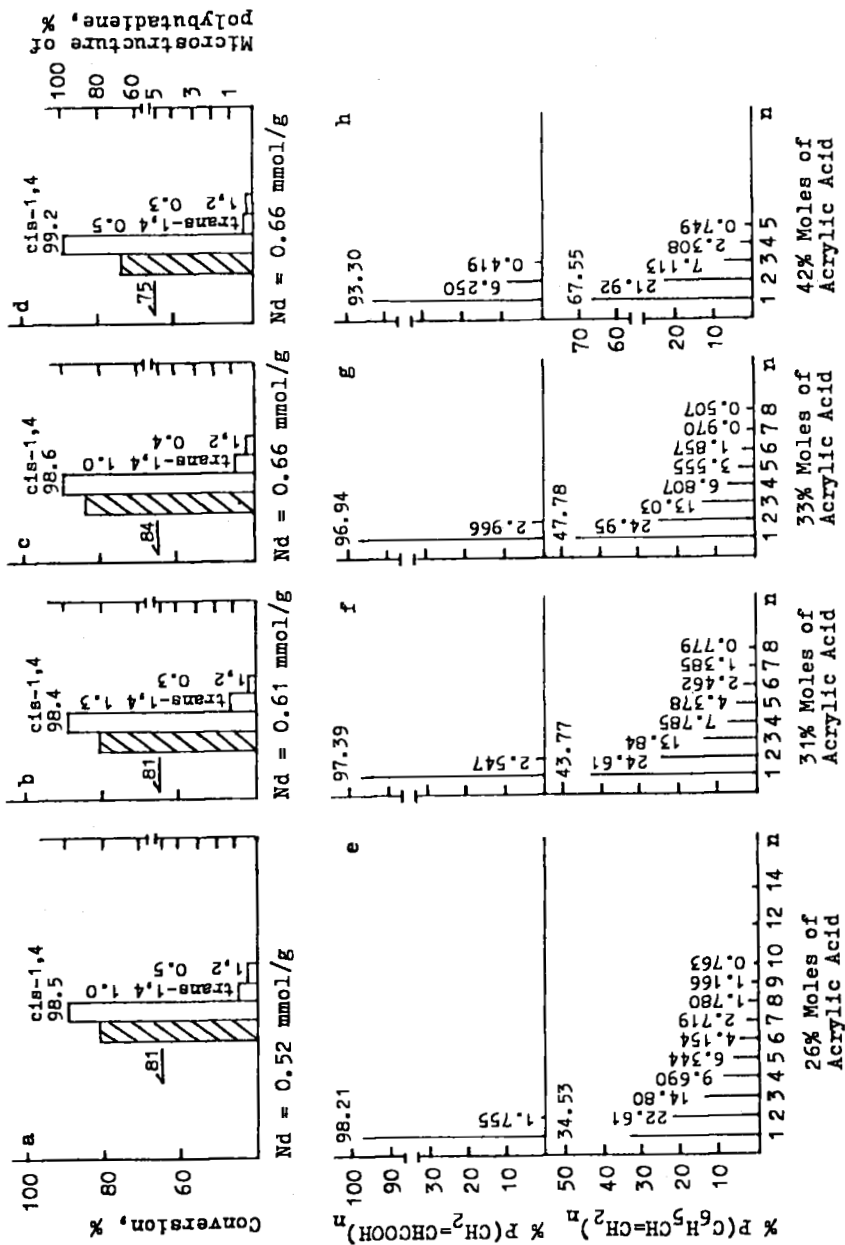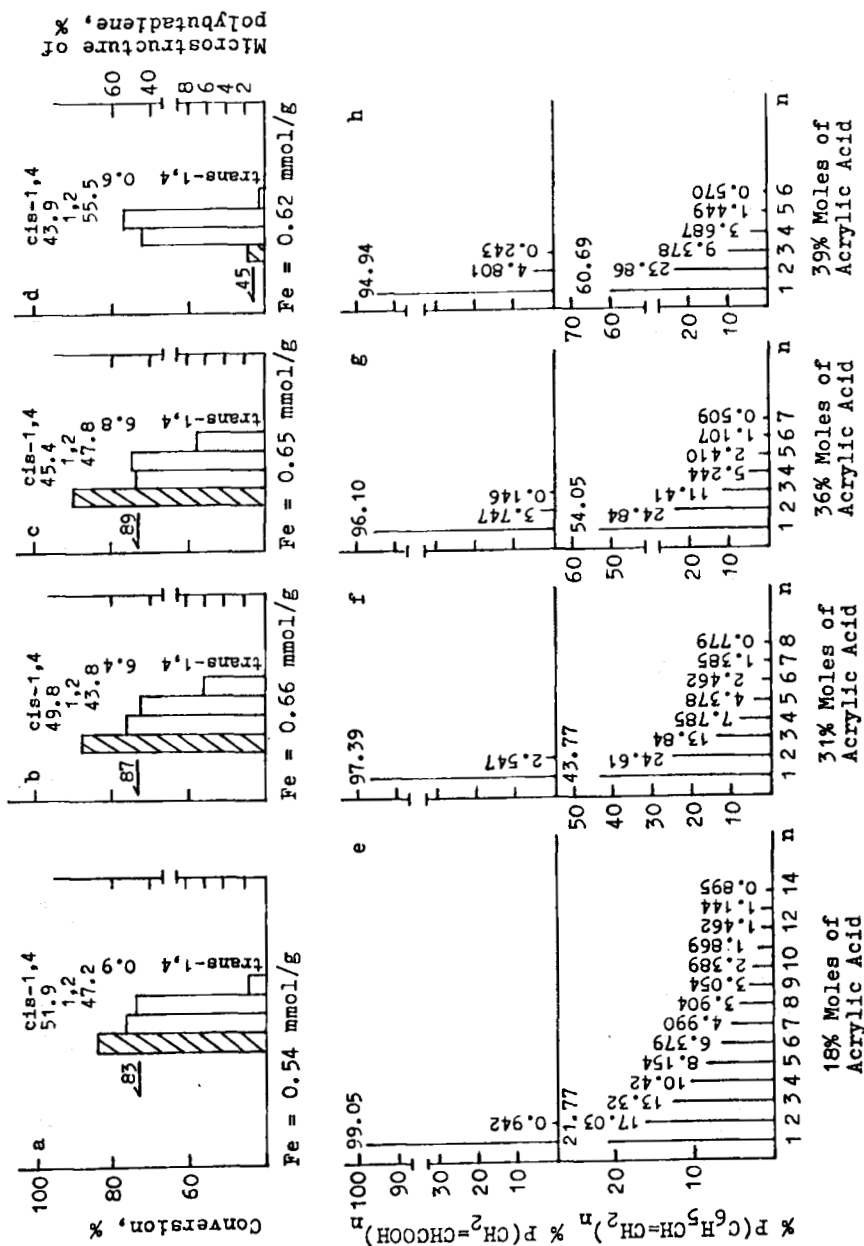
% P(C₆H₅CH=CH₂)ₙ % P(CH₂=CHCOOH)

FIG. 3. Distribution function of sequences of different lengths in SAAC having different compositions and activity of SAAC · Fe. Polymerization conditions: (a–d) Fe/Bd = 1 μmol/g; third component, phenanthroline; phenanthroline/Fe molar ratio = 0.7; cocatalyst, Al(i-C₄H₉)₃; Al/Fe molar ratio = 70; 20°C; 30 min.

plexes supported on polymer (V), or on polymer (VI), is also related to the unsuitable distribution of the carboxyl groups on the surface of the polymers. Figure 2 shows that for 33% mol acrylic acid where the distribution of long (for n between 2 and 8) and short sequences of styrene in the copolymer is nearly equal, the activity of the neodymium complex is maximized. It is clear that the spatial distribution of the neodymium ions in SAAC · Nd is favorable for the formation of active centers. This regularity not only appears in the neodymium system producing high *cis*-1,4-polybutadiene, but also in the iron system producing the polybutadiene with an approximately equal distribution of *cis*-1,4- and 1,2-structures (Figs. 3a–d). The quantity of bound iron in the iron complexes, corresponding to the copolymers containing 18, 31, 36, and 39% mole acrylic acid (Figs. 3e–h), was 0.54, 0.66, 0.65, and 0.62 mmol/g (Figs. 3a–d), respectively. When the value of the distribution function for short sequences of styrene is 54%, the catalytic activity of the iron complex supported on styrene–acrylic acid copolymer is optimum.

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