778. *Anionic Polymerisation of Vinyl Monomers with Butyl-lithium.*

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The anionic polymerisation of various vinyl monomers by use of butyl-lithium was investigated. The effects of concentration of catalyst, temperature, and solvents were studied.

THE polymerisation of isoprene by butyl-lithium has recently been extensively studied.[1] In heterogeneous systems under certain conditions stereospecific polymerisation occurs giving polymers of regular structure, *e.g.*, *cis*-1,4-polyisoprene. We have now studied the polymerisation of methyl methacrylate, acrylonitrile, styrene, and other vinyl monomers using n-butyl-lithium as catalyst. All these monomers have electronegative substituents and are susceptible to anionic polymerisation.

Polymerisation of Methyl Methacrylate.—This was investigated in light petroleum, a non-polar solvent of low dielectric constant, which is a good solvent for the monomer even at low temperature. The polymer, being insoluble, was precipitated on formation.

The dependence of yield of the poly(methyl methacrylate) on the amount of catalyst was investigated. Experiments were carried out (Table 1) with identical quantities and concentrations of methyl methacrylate in light petroleum at —15°. Butyl-lithium, in the

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[1] Hsieh and Tobolsky, *J. Polymer Sci.*, 1957, **25**, 245; Morita and Tobolsky, *J. Amer. Chem. Soc.*, 1957, **79**, 5853.

same solvent, was added in one portion with mechanical stirring; the polymerisation time was 1 hr. throughout. A threshold concentration of catalyst was needed to start the polymerisation, but there was no induction period. The yield increased with increasing amount of catalyst to approximately quantitative values. The molecular weights obtained were high (about 130,000) and did not depend on the amount of catalyst (Table 1). Somewhat lower yields were obtained on adding the monomer dropwise to the catalyst during 15 min. under otherwise constant conditions, so that a small initial concentration of monomer existed (Table 1). Yields did not change either on extending the time of addition from 15 min. to 60 min. or on addition of catalyst to monomer during 15 min.

TABLE 1. *Polymerisation of methyl methacrylate. Dependence of polymerisation yield on amount of catalyst.*

Experimental Conditions.—Butyl-lithium dissolved in light petroleum (15 ml.) was added in one portion to cooled methyl methacrylate (25 ml.; 2·34 moles/l.) in light petroleum (60 ml.). Polymerisation temperature −15°, time 1 hr.

Catalyst (mmole)	2	3	4	4·5	6	8	10	12	15
[Catalyst] (M)	0·02	0·03	0·04	0·045	0·06	0·08	0·1	0·12	0·15
Polymer (g.)	Trace	Trace	2·5	8·5	17 [a]	18	21 [bc]	22 [d]	22
Yield (%)	—	—	11	36	73	77	90	94	94
$[\eta]$ (dl./g.)	—	—	—	—	0·29	0·29	—	—	0·27
$10^{-3}M$ *	—	—	—	—	128	128	—	—	116

* Average molecular weights of the polymers were calculated from intrinsic viscosities, measured in toluene at 30°, by use of the equation $[\eta] = 6{\cdot}87 \times 10^{-5}M^{0{\cdot}71}$ (Riddle, "Monomeric Acrylic Esters," Reinhold, New York, 1954, p. 64).

[a] Monomer added during 15 min. under otherwise constant conditions gave 12 g. (52%) of polymer.

[b] Monomer added during 15 min. under otherwise constant conditions gave 17 g. (73%) of polymer.

[c] Catalyst dissolved in 25 ml. of light petroleum, added during 15 min. to monomer in light petroleum (50 ml.) under otherwise constant conditions gave 17 g. (73%) of polymer. [d] Catalyst in light petroleum (15 ml.) added to monomer in benzene under the above conditions, gave 4 g. (17%) of polymer, obtained on evaporation of solvent. Similar yields were obtained with tetrahydrofuran or ether.

The progress of the polymerisation, followed under otherwise constant conditions (Table 2), was fast at first; in 10 min. about half the yield was obtained. In the last 30 min. the polymerisation was slow and the yield increased by only 10%.

The effect of temperature was investigated between −30° and +50° (Table 3); increase in temperature lowers the yield. Thus, polymerisation at 50° gave only about 25% of the yield of that at −15°. The increase in yield at low temperature may be due to the enhanced stability of the carbanionic propagation centres. The polymers obtained at lower temperature had higher molecular weights (Table 3).

TABLE 2. *Polymerisation of methyl methacrylate. Dependence of yield on polymerisation time.*

Experimental Conditions.—As in Table 1, except that butyl-lithium (6×10^{-3} mole; 0·06 mole/l.) was used throughout and polymerisation carried out for the time stated.

Time (min.)	5	10	15	20	30	60
Polymer (g.)	3	8 *	11	14	15·5	17
Yield (%)	13	34	47	60	67	73

* This polymer gave an intrinsic viscosity of 0·25 dl./g. corresponding to $M = 104{,}000$.

TABLE 3. *Polymerisation of methyl methacrylate. Dependence of yield on polymerisation temperature.*

Experimental Conditions.—As in Table 1, except that butyl-lithium (8×10^{-3} mole; 0·08 mole/l.) was used throughout and the polymerisation carried out at different temperatures.

Temperature [a]	−30°	−15°	30°	50°
Polymer (g.)	18	18 [b]	12·5 [c]	3·5
Yield (%)	77	77	54	15

[a] A smaller amount of catalyst being used (6×10^{-3} mole; concn. 0·06 mole/l.), the polymerisation was more affected by increase in temperature. Thus polymerisation at 10° gave 10 g. of polymer compared with 17 g. at −15°. [b] $[\eta] = 0{\cdot}29$ dl./g.; $M = 128{,}000$. [c] $[\eta] = 0{\cdot}2$ dl./g.; $M = 76{,}000$.

Preliminary polymerisations in ether, benzene, or tetrahydrofuran (Table 1), *i.e.*, solvents in which the polymer was soluble, gave very low yields even at high concentrations of catalyst.

X-Ray diffraction diagrams of two samples of poly(methyl methacrylate) [one prepared with 0·004 mole of butyl-lithium at —15° (Table 1) and the other with 0·008 mole of butyl-lithium at —50°], pressed in a Carver press at 120°/2000 lb./in.$^{-2}$ and swelled in ether, showed partial crystallinity. Three broad reflection bands appeared having *d*-values of 6·0 ± 0·4 Å (very strong), 2·85 ± 0·15 Å (medium), and 2·5 ± 0·15 Å (weak). The strong reflection can be indexed as an *hkl* reflection (020) on the basis of the unit cell suggested for syndiotactic poly(methyl methacrylate).[2]

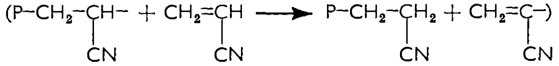
TABLE 4. *Polymerisation of acrylonitrile. Dependence of polymerisation yield on amount of catalyst.*

Experimental Conditions.—Butyl-lithium dissolved in light petroleum (15 ml.) was added in one portion to cooled acrylonitrile (25 ml.; 3·77 mole/l.) in light petroleum (60 ml.). Polymerisation temperature —15°, time 1 hr.

Catalyst (mmole)	1	1·5	2	2·5	3	4	6	10	12
[Catalyst] (mole/l.)	0·01	0·015	0·02	0·025	0·03	0·04	0·06	0·1	0·12
Polymer (g.)	2	2·5	3·5	5	6[a]	9[d]	15	16[e]	18[bc]
Yield (%)	10	13	18	25	30	45	75	80	90
[η] (dl./g.)	0·44	—	—	—	—	0·4	—	—	0·37
$10^{-3}M$ *	23·5	—	—	—	—	21	—	—	18·5

* Average molecular weights of the polymers were calculated from intrinsic viscosities measured in dimethylformamide at 30° by use of the equation $[\eta] = 2{\cdot}33 \times 10^{-4}M^{0{\cdot}75}$ (Cleland and Stockmayer, *J. Polymer Sci.*, 1955, **17**, 473).

[a] Monomer added during 15 min. under otherwise constant conditions gave 2 g. of polymer.
[b] Monomer added during 15 min. under otherwise constant conditions gave 15·5 g. (78%) of polymer; [η] = 0·36 dl./g.; M = 18,000. In this case there was a smaller concentration of monomer in the beginning of the polymerisation; nevertheless the molecular weight of the polymer was the same, showing that the degree of polymerisation was independent of the concentration of the monomer and that the termination reaction is dominated by chain transfer with monomer (ref. 3, p. 223):



$$(\mathrm{P{-}CH_2{-}}\underset{\displaystyle\mathrm{CN}}{\mathrm{CH}}{-} + \mathrm{CH_2{=}}\underset{\displaystyle\mathrm{CN}}{\mathrm{CH}} \longrightarrow \mathrm{P{-}CH_2{-}}\underset{\displaystyle\mathrm{CN}}{\mathrm{CH_2}} + \mathrm{CH_2{=}}\underset{\displaystyle\mathrm{CN}}{\mathrm{C}}{-})$$

[c] Ether being used as solvent instead of light petroleum, the yield was 7 g. (35%) of polymer; [η] = 0·11 dl./g.; M = 3750. [d] Catalyst dissolved in light petroleum (15 ml.) was added to monomer in tetrahydrofuran (60 ml.) gave 3 g. of polymer; [η] = 0·18 dl./g.; M = 7000. [e] Catalyst dissolved in light petroleum (15 ml.) was added to monomer in tetrahydrofuran (60 ml.) gave 7 g. (35%) polymer; [η] = 0·14 dl./g.; M = 5000.

Polymerisation of Acrylonitrile.—The dependence of yield of the polyacrylonitrile on the amount of catalyst was investigated. Comparable experiments were carried out (Table 4) in light petroleum at a constant temperature of —15°. The catalyst, in the same solvent, was added in one portion and the polymerisation was carried on for 1 hr. The acrylonitrile is only slightly soluble in light petroleum at —15° and so two liquid phases were formed during the polymerisation. A threshold concentration of catalyst was needed to start the polymerisation but this was less than in the case of methyl methacrylate. This might be due to the presence of the nitrile group which is much more electronegative than the ester group. The molecular weights of the polymers were generally much lower than those of poly(methyl methacrylate). The reactive α-hydrogen atom of the acrylonitrile can enter into chain transfer reactions which lower the molecular weight. Molecular weight did not depend on the amount of catalyst. Other polymerisation experiments carried out by addition of monomer to catalyst during 15 min. (Table 4) under otherwise constant conditions gave somewhat lower yields especially with small amounts of catalyst.

Temperature had a pronounced effect on polymerisation (Table 5). Thus a polymerisation at 10° gave less than 50% of the yield of a similar one at —15°. The molecular weights of the polymers obtained at lower temperature were much higher owing to the

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[2] Stroupe and Hughes, *J. Amer. Chem. Soc.*, 1958, **80**, 2341.

TABLE 5. *Polymerisation of acrylonitrile. Dependence of yield on polymerisation temperature.*

Experimental Conditions.—As in Table 4, except that butyl-lithium (4 × 10^{-3} mole; 0·04 mole/l.) was used and the polymerisation carried out at different temperatures.

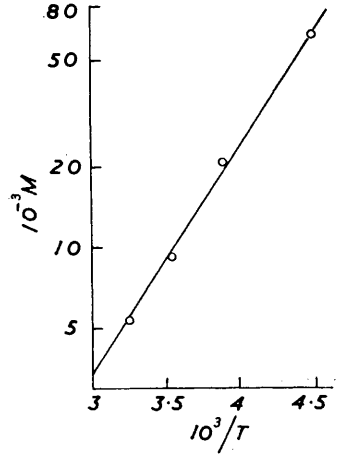
Temperature	−50°	−15°	10°	35°
Polymer (g.)	6	9	4	2·5
Yield (%)	30	45	20	13
[η] (dl./g.)	0·94	0·4	0·22	0·15
$10^{-3}M$	64	21	9·25	5·5

decreased effect of chain transfer. A semi-logarithmic plot (Figure) of molecular weight against the reciprocal of the polymerisation temperature for acrylonitrile gave a straight line, whose slope [3] corresponds to a difference in activation energy between propagation and termination of 4 kcal./mole.

Polymerisations in tetrahydrofuran or ether instead of light petroleum gave lower yields and the polymers had lower molecular weights (Table 4).

X-Ray diffraction diagram of a sample of polyacrylonitrile prepared at −50° (Table 5) showed two broad reflections having *d*-values of 5·55 ± 0·4 Å (strong), 3·4 ± 0·3 Å (medium). The spacing of 5·3 Å is associated with the distance between chains through the hydrogen-bonded nitrile groups.[4] The second reflection is absent from ordinary undrawn polyacrylonitrile preparations.

Polymerisation of Styrene.—The anionic polymerisation of styrene with butyl-lithium was markedly different from those of methyl methacrylate or acrylonitrile. The same experimental conditions being used as for the latter monomers [catalyst (0·01 mole) added to styrene (1 vol.) in light petroleum (3 vol.) at −15°], a light brown colour appeared owing to the formation of styryl carbanions, but no significant polymerisation had occurred after 1 hr. Carbonation of the product with solid carbon dioxide showed that most of the butyl-lithium remained unchanged and was converted into valeric acid. Doubling the amount of catalyst (0·02 mole) did not induce significant polymerisation (Table 6, *A*). In other experiments styrene was added dropwise during 15 min. to the catalyst dissolved in light petroleum (3 vol.) at −15° so that a great initial concentration of catalyst existed; here also only slight polymerisation occurred. A higher temperature increased the polymerisation considerably, and when the temperature was increased to 50° the styrene polymerised completely to a heavy red oil which solidified under light petroleum. These experiments show that the styrene, having a weak electronegative group (phenyl) needs a high activation energy for initiation of the polymerisation, unlike the previous monomers. No activation energy is necessary for propagation [5] as this involves the approach of an ion to a neutral molecule in light petroleum which has a low dielectric constant.



Molecular weight of polyacrylonitrile as a function of temperature.

In both ether and tetrahydrofuran styrene polymerised at −15°. This may be due to solvation of the catalyst (the lithium cation yielding the green complex with the tetrahydrofuran owing to the formation of an electron octet by means of co-ordination valencies with the oxygen atom [6]). This apparently lowers the activation energy of the initiation.

On the other hand it was possible to polymerise pure styrene even with very small

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[3] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953, p. 218.

[4] Schildknecht, " Vinyl Polymers," Wiley, New York, 1952, p. 276.

[5] Billmeyer, " Polymer Chemistry," Interscience, New York, 1957, p. 267.

[6] Uelzmann, *J. Polymer Sci.*, 1958, **32**, 457.

TABLE 6. *Polymerisation of styrene.*

A. Experimental Conditions.—Polymerisations were carried out in a three-necked flask with 25 ml. of styrene (0·218 mole) under the conditions indicated below; polymerisation time, 1 hr.

Solvent for monomer (ml.)	Solvent for catalyst (ml.)	[Styrene] (M)	Butyl-lithium (mmole)	[Butyl-lithium] (M)	Temp.	Polymer (g.)	Yield (%)
Pet (60)	Pet (15)	2·18	10	0·1	−15°	Trace [a,b]	
Pet (50)	Pet (25)	2·18	20	0·2	−15	Trace [c]	
Pet (60)	Pet (15)	2·18	10	0·1	0	4	(18%) [d]
Pet (25)	Pet (50)	2·18	12	0·12	40	22	(97%) [e]
Pet (25)	Pet (30)	2·73	10	0·15	50	22	(97%) [f,g]
Ether (50)	Pet (35)	1·98	20	0·182	−15	19	(84%) [c,i]
Ether (50)	Pet (15)	2·42	11	0·122	0	21	(93%) [c,h]
None	Ether (10)		10		−10	22	(97%) [j]
Tet (60)	Pet (15)	2·18	5	0·05	−15	10	(44%) [b]
Tet (60)	Pet (15)	2·18	10	0·1	−15	22	(97%) [c]

Pet = light petroleum. Tet = tetrahydrofuran.

[a] Trace indicates the formation of 1 g. of polymer or less. [b] Catalyst added to monomer in one portion. [c] Cooled catalyst added during 3 min. [d] $[\eta] = 0{\cdot}049$ dl./g.; $M = 2300$. Molecular weights were calculated according to the equation of Waack *et al.* (Ref. 9). $[\eta] = 1{\cdot}6 \times 10^{-4}M^{0{\cdot}74}$. [e] Monomer added to catalyst during 30 min. [f] Catalyst added to monomer at −10°, then reaction mixture was heated to 50°. [g] $[\eta] = 0{\cdot}048$ dl./g.; $M = 2200$. This is in good agreement with the molecular weight calculated from the formula:

$$\frac{\text{Moles of styrene} \times \text{Molecular weight of styrene}}{\text{Moles of catalyst}} = \frac{0{\cdot}218 \times 104}{0{\cdot}01} = 2265$$

[h] $[\eta] = 0{\cdot}043$ dl./g.; $M = 1900$. [i] $[\eta] = 0{\cdot}031$ dl./g.; $M = 1200$. [j] Styrene was added slowly to catalyst to prevent uncontrollable polymerisation.

B. Experimental Conditions.—Polymerisations carried out at room temperature in a 500 ml. wide-mouthed bottle. The butyl-lithium was added in one portion from a pipette to undiluted styrene (20 ml.); catalyst was added until sudden polymerisation of the styrene occurred.

Catalyst (mmole)	2	6	7·6
Solvent for catalyst (ml.)	Ether (3)	Ether (9)	Pet (6)
Time of addition (sec.)	4	10	8
Polymer (g. and % yield)	14 (77%)	16 (88%)	16 (88%)

amounts of catalyst if this was added within a few seconds as a concentrated solution (Table 6, *B*). The heat generated locally will greatly further the initiation step and cause very rapid polymerisation of the monomer. In these reactions, the styrene " flash "-polymerised completely and the temperature soared to 110°, indicating the strong exothermic polymerisation. Addition of the catalyst during a comparatively larger time interval enables the reaction heat to dissipate and more catalyst is needed for complete polymerisation. In these " flash "-polymerisations the polymerising styrene expanded to a large volume and yielded a friable mass reminiscent of foam polymerisation products, the low-boiling solvents (ether or light petroleum) serving as the blowing agents.

An important feature of the polymerisation of styrene is that the polymer obtained is dull red owing to the presence of carbanion end-groups, showing that no termination step has occurred and thus " living polymers " [7] are obtained. These are similar to the living polymers prepared by Szwarc, Levy, and Milkovich by electron-transfer catalysts in non-proton donating solvents.[7] The polymers, possessing still intact carbanion propagation centres, polymerise other freshly added monomers such as styrene, methyl methacrylate, or acrylonitrile and thus produce block polymers (see Experimental). On being exposed to air, or on addition of alcohol or water, the colour disappeared completely as the carbanions were destroyed. These polymers reacted with Michler's ketone in benzene under the conditions of the Gilman and Schultze's test [8] for organometallic compounds; however the characteristic green colour developed only after several hours' standing, unlike those given by simple organometallic compounds such as butyl-lithium. From the benzene solution it was possible to precipitate a green polystyrene with methanol.

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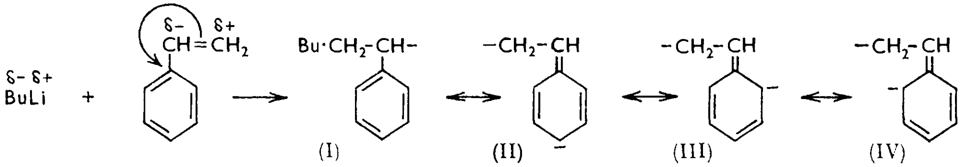
[7] Szwarc, Levy, and Milkovich, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

[8] Gilman and Schultze, *J. Amer. Chem. Soc.*, 1925, **47**, 2002; Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, Green & Co., London, 1956, p. 241.

A characteristic of " living " polymers is that the molecular weight[9] depends only on the ratio of the monomer to the catalyst, more catalyst proportionately decreasing the molecular weight, and is independent of temperature. The " living " polymers (Table 6, *A*) show such behaviour. Block copolymers can be produced, having polystyrene of the required molecular weight, by varying the quantity of the catalyst and carrying the polymerisation of the styrene to completion before adding other monomers.

The absence of the termination step from the polymerisation of styrene by butyl-lithium is plausible for the following reasons: (*a*) The polymerisations were carried out in non-proton donating solvents such as light petroleum, so that no termination will occur by abstraction of a proton from the solvent. (b) The styryl carbanions are resonance-stabilised by the benzene ring and four resonance structures are possible (I—IV).



Polymerisation of Other Monomers.—Some experiments on the polymerisation of methyl acrylate, butyl acrylate, allyl acetate, vinyl acetate, and dimethyl maleate with butyl-lithium were carried out. In all cases, variation of the amounts of catalyst and polymerisation temperatures gave only viscous or semi-solid polymers in low yields.

EXPERIMENTAL

Materials.—Light petroleum (b. p. 60—80°), ether, tetrahydrofuran, and benzene were dried (Na), and boiled under nitrogen before use. Methyl methacrylate, acrylonitrile, methyl acrylate, and vinyl acetate were dried and distilled under nitrogen. Styrene was distilled over sulphur. Nitrogen was freed from oxygen by passage through a quartz tube containing fresh copper wire at 600°, then through a 5% alkaline permanganate solution followed by a solution of 20% pyrogallol in 20% sodium hydroxide, and dried (conc. H_2SO_4). n-Butyl-lithium, prepared as before,[10] was kept in an ice-box and its concentration in the solvent checked by titration before use.

Polymerisation of Monomers.—The addition of reagents and the polymerisations were carried out under nitrogen. Into a three-necked flask fitted with a high-speed stirrer, dropping funnel, and a gas-adapter for introducing nitrogen, the required amounts of monomer and solvent were added. The flask was cooled to the required temperature and kept thereat. The catalyst solution was then added. The polymerisation was stopped after the required time by adding 50 ml. of cooled hydrochloric acid (10%). The polymer was filtered off, washed with water, light petroleum, and methanol to remove monomer, and then dried to constant weight in a vacuum-desiccator at room temperature or in an electric oven at 60°.

" Flash "-polymerisation of styrene, in which the catalyst solution was added during several seconds to the undiluted monomer, was carried out in wide-mouthed Pyrex bottles and the catalyst added from a pipette.

Viscosities of polymer solutions were measured in an Ostwald or an Ostwald–Fenske viscosimeter.

Preparation of a Block Polymer of Styrene–Acrylonitrile.—" Living " polymer of styrene was prepared by the rapid addition of a concentrated solution of butyl-lithium in ether. The polymer, obtained as a dull red mass, gave a negative Gilman–Schultze test for organometallic compounds, indicating absence of residual butyl-lithium.

0·3 g. of this polymer was added to 4 ml. of distilled acrylonitrile in a test-tube flushed with nitrogen. Polymerisation started immediately with evolution of heat, and the polystyrene particles became covered with brown-red polyacrylonitrile. After 2 hr. the polymer was filtered off, washed with light petroleum, then with water to remove lithium salts, and dried

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[9] Waack, Rembaum, Coombes, and Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 2026.

[10] Frankel, Rabani, and Zilkha, *J. Polymer Sci.*, 1958, **28**, 387.

in vacuo. The polymer was purified by boiling it in benzene. This removed all the polystyrene and block polymers low in acrylonitrile, leaving 0·35 g. of insoluble polymer. When this was boiled with acetone, 0·09 g. of a reddish-brown insoluble polymer remained. Evaporation of the acetone *in vacuo* gave 0·23 g. of block polymer, analysis of which gave 16·6% of nitrogen, showing it to consist of 63% of acrylonitrile and 37% of styrene. It was insoluble in chloroform or dioxan, and melted at *ca.* 190—200° (decomp.).

The polymer insoluble in acetone gave on analysis 21% of nitrogen, showing it to consist of 80% of acrylonitrile and 20% of styrene. It decomposed at *ca.* 220—230°. This block polymer might be contaminated with free polyacrylonitrile, if any such polymer was formed during the polymerisation by chain transfer.

Infrared spectra of the block polymer showed absorption at 4·45 μ (cyanide group of the polyacrylonitrile) and at 6·2 μ, 6·65 μ, and 13·4 μ (aromatic ring of polystyrene).

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